

IChO 1982

Theory problems and solutions · Stockholm, Sweden · 7 theory problems with complete solutions

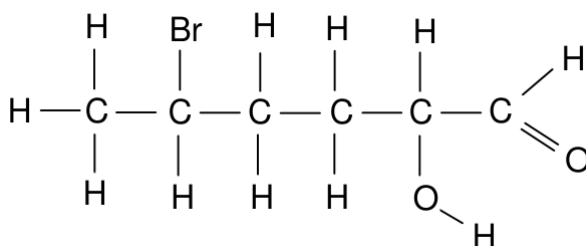
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Problem 1: Ten short questions A-K (mostly multiple choice)

A. The IUPAC name of the compound $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ is

- a) cobalt(II) hexaammonia dichlorine,
- b) cobalt(II) hexaammonia dichloride,
- c) hexaammincobalt(II) chloride.
- d) hexaamminedichlorocobalt(II)
- e) cobalt(II) chloride-hexaammonia

B. The IUPAC name of the compound



is:

- a) 5-bromo-1-hexanoic acid
- b) 5-bromo-2-hydroxy-1-hexanal
- c) 2-bromo-5-hydroxy-6-hexanal
- d) 2-bromo-2-hydroxy-1-hexanal
- e) 5-bromo-2-hydroxy-1-hexanone

C. Which of the following acid-base pairs is most suitable for keeping the pH constant at 9 in an aqueous solution?

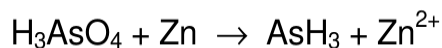
- a) $\text{CH}_3\text{COOH} - \text{CH}_3\text{COO}^-$
- b) $\text{NH}_4^+ - \text{NH}_3$
- c) $\text{H}_2\text{CO}_3 - \text{HCO}_3^-$
- d) $\text{H}_2\text{PO}_4^- - \text{HPO}_4^{2-}$
- e) $\text{H}_2\text{C}_2\text{O}_4 - \text{HC}_2\text{O}_4^-$

D. One of the following statements cannot be correct. State which one.

- a) A water-soluble solid contains Mg^{2+} , Cr^{3+} , and Br^- .
- b) A solid soluble in a sodium hydroxide solution contains Al^{3+} , K^+ , and SO_4^{2-} .
- c) A solid soluble in aqueous ammonia solution contains Ag^+ , Cu^{2+} , and Cl^- .

- d) A solid soluble in nitric acid contains Ba^{2+} , Fe^{2+} , and CO_3^{2-} .
 e) A solution neutral to litmus contains Na^+ , Ca^{2+} , and PO_4^{3-} .

E. Complete the following equation:



The reaction is carried out in an acid solution. Fill in the missing particles and balance the reaction equation.

F. State the degree of protolysis of acetic acid with concentration of 0.25 mol dm^{-3} .

$$K_a(\text{HAc}) = 1.8 \times 10^{-5}.$$

- a) 0.021 %; b) 0.21 %; c) 0.84 %; d) 1.3 %; e) 8.4 %

G. A solution with a volume of 1.00 dm^3 is saturated with lead iodide, PbI_2 . The concentration of iodide ions is 2.7 mol dm^{-3} . Determine the solubility product of PbI_2 .

- a) 3.6×10^{-6} ; b) 2.0×10^{-8} ; c) 9.8×10^{-9} ; d) 2.5×10^{-9} ; e) 4.9×10^{-9} .

H. The following standard enthalpies of formation are given:

Compound	ΔH^0
Acetic acid	$-0.50 \text{ MJ mol}^{-1}$
Carbon dioxide	$-0.40 \text{ MJ mol}^{-1}$
Water	$-0.30 \text{ MJ mol}^{-1}$

The ΔH^0 of combustion of acetic acid is:

- a) 0.90 MJ mol^{-1} ; b) $-0.90 \text{ MJ mol}^{-1}$; c) $-0.20 \text{ MJ mol}^{-1}$;
 d) -2.1 MJ mol^{-1} ; e) 0.20 MJ mol^{-1}

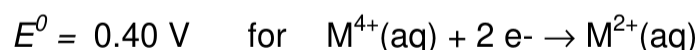
I. $\text{COCl}_2(\text{g})$ is introduced in an empty vessel at a pressure of a . It dissociates and the following equilibrium is established at constant temperature:



If x represents the partial pressure of $\text{CO}_2(\text{g})$ at equilibrium, what is the equilibrium expression?

- a) $\frac{4x^3}{(a-2x)^2} = K_p$
 b) $\frac{2x^4}{(a-2x)^2} = K_p$
 c) $\frac{2x^3}{(a-x)^2} = K_p$
 d) $\frac{4x^3}{(a-x)^2} = K_p$
 e) $\frac{x^3}{(a-3x)^2} = K_p$

K. For a metal M the following redox data are known:



The E^0 for $\text{M}^{4+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{M}^+(\text{aq})$ is then:

a) -0.20 V b) -1.00 V c) 1.00 V d) 0.07 V e) -0.07 V

Official English text of the problem.

Answers

- **A. c)** Hexaamminecobalt(II) chloride, $[\text{NH}_3] \rightarrow [\text{Co}+2] (<-\text{[NH}_3]) (<-\text{[NH}_3]) (<-\text{[NH}_3]) (<-\text{[NH}_3]) (<-\text{[NH}_3]) (<-\text{[NH}_3]) \cdot [\text{Cl}-] \cdot [\text{Cl}-]$.
- **B. b)** 5-Bromo-2-hydroxyhexanal, $\text{CC}(\text{Br})\text{CCC}(\text{O})\text{C}=\text{O}$; stereochemistry is unspecified.
- **C. b)** Ammonium $[\text{NH}_4+]$ / ammonia N.
- **D. e)** The statement about the solution neutral to litmus.
- **E.** $\text{H}_3\text{AsO}_4 + 4 \text{Zn} + 8 \text{H}^+ \rightarrow \text{AsH}_3 + 4 \text{Zn}^{2+} + 4 \text{H}_2\text{O}$.
- **F. c)** $\alpha = 0.84\%$.
- **G.** As printed, the concentration product is $9.8 \text{ mol}^3 \text{ dm}^{-9}$, matching **none** of the options. If the intended iodide concentration is $2.7 \times 10^{-3} \text{ mol dm}^{-3}$, the answer is **c)**, $9.8 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$.
- **H. b)** $\Delta_c H^\circ = -0.90 \text{ MJ mol}^{-1}$.
- **I. a)** $K_p = \frac{4x^3}{(a-2x)^2}$, using the pressure convention of the choices.
- **K. d)** $E^\circ = +0.07 \text{ V}$.

Solution

SMILES for salts specify their ionic components, rather than their crystal lattices. The coordination-complex SMILES use the dative-bond extension, with arrows pointing from ligand to metal.

A. Coordination-compound nomenclature

The two chloride counterions, chloride $[\text{Cl}-]$, require the complex cation to carry charge $+2$. Each ammonia ligand, ammonia N, is neutral, so cobalt has oxidation state $+2$:

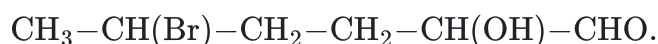
$$z_{\text{Co}} + 6(0) + 2(-1) = 0 \quad \Rightarrow \quad z_{\text{Co}} = +2.$$

Coordinated ammonia is named **ammine**. Six such ligands give **hexaammine**; the metal name and oxidation state follow, and the counterion is named last. Thus the name is **hexaamminecobalt(II) chloride**, option **c**.

The six nitrogen donors form an octahedral coordination sphere. The chloride ions lie outside that sphere; the SMILES does not itself specify its octahedral geometry.

B. Organic nomenclature

The structure is



The aldehyde group has priority over the alcohol group and determines the suffix **-al**. Its carbon is carbon 1. The six-carbon chain is therefore numbered as follows:

- C1: aldehyde carbon;
- C2: hydroxy substituent;
- C5: bromo substituent.

The prefixes are written alphabetically, giving **5-bromo-2-hydroxyhexanal**, $\text{CC}(\text{Br})\text{CCC}(\text{O})\text{C}=\text{O}$.

This corresponds to option **b**, whose wording includes the unnecessary aldehyde locant "1". Both C2 and C5 are stereogenic, but the drawing specifies neither configuration; consequently, no stereochemical markers belong in the SMILES.

C. Buffer selection

For a weak acid and its conjugate base,

$$\text{pH} = \text{p}K_{\text{a}} + \log_{10} \left(\frac{[\text{conjugate base}]}{[\text{acid}]} \right).$$

A buffer works most effectively when both forms are present in substantial amounts, which occurs near $\text{pH} = \text{p}K_{\text{a}}$.

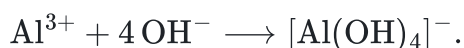
Of the listed pairs, **ammonium/ammonia** has its acid $\text{p}K_{\text{a}}$ nearest pH 9. Ammonia consumes added acid, while ammonium consumes added base. Therefore the best choice is **b**.

D. Compatibility of the stated ions

The intended answer is **e**, under the usual qualitative-analysis assumption that the named ions are present in appreciable concentrations.

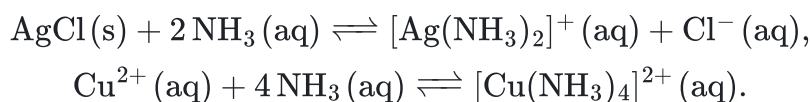
The other statements are chemically possible:

- **a)** Magnesium(II) $[\text{Mg}^{+2}]$, chromium(III) $[\text{Cr}^{+3}]$, and bromide $[\text{Br}^-]$ can occur in water-soluble bromide salts.
- **b)** Aluminium(III) $[\text{Al}^{+3}]$, potassium $[\text{K}^+]$, and sulfate $[\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$ can occur together in a sulfate salt. In excess hydroxide, hydroxide $[\text{OH}^-]$, aluminium forms soluble tetrahydroxoaluminate(III), $\text{O}[\text{Al}^-](\text{O})(\text{O})\text{O}$:



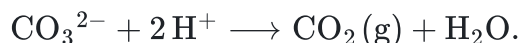
The aluminate ion has tetrahedral coordination.

- **c)** Silver(I) $[\text{Ag}^+]$ and copper(II) $[\text{Cu}^{+2}]$ form soluble ammine complexes in excess ammonia:



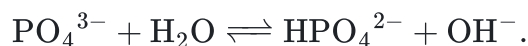
The complexes are diammine silver(I), $[\text{NH}_3] \rightarrow [\text{Ag}^+] \leftarrow [\text{NH}_3]$, and tetraamminecopper(II), $[\text{NH}_3] \rightarrow [\text{Cu}^{2+}] (\leftarrow [\text{NH}_3]) (\leftarrow [\text{NH}_3]) \leftarrow [\text{NH}_3]$. The silver complex is linear. In the aqueous copper complex, the four ammonia donors occupy approximately square equatorial positions, with water ligands completing the coordination sphere; these waters are omitted from the abbreviated formula and SMILES.

- **d)** Barium(II) $[\text{Ba}^{2+}]$ and iron(II) $[\text{Fe}^{2+}]$ carbonates dissolve in acid because carbonate, $[\text{O}^-] \text{C}(=\text{O}) [\text{O}^-]$, is protonated:

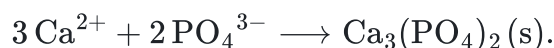


Here hydrogen ion is $[\text{H}^+]$, carbon dioxide is $\text{O}=\text{C}=\text{O}$, and water is O . Nitric acid, $\text{O}=[\text{N}^+]([\text{O}^-])\text{O}$, may also oxidize iron(II), but this does not contradict the composition of the original solid or its dissolution.

For **e**, sodium $[\text{Na}^+]$ is a spectator, but orthophosphate, $[\text{O}^-] \text{P}(=\text{O}) ([\text{O}^-]) [\text{O}^-]$, hydrolyses to produce hydroxide:



The hydrogen phosphate ion is $\text{OP}(=\text{O}) ([\text{O}^-]) [\text{O}^-]$. Appreciable orthophosphate therefore makes the solution alkaline. Furthermore, calcium(II), $[\text{Ca}^{2+}]$, precipitates phosphate:



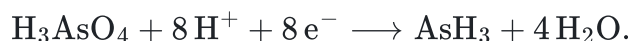
These properties conflict with the proposed neutral solution containing appreciable amounts of both calcium and orthophosphate ions.

E. Redox balancing in acidic solution

The arsenic-containing species are arsenic acid, $\text{O}=[\text{As}](\text{O})(\text{O})\text{O}$, and arsine, $[\text{AsH}_3]$.

Arsenic changes from oxidation state +5 in H_3AsO_4 to -3 in AsH_3 , gaining eight electrons.

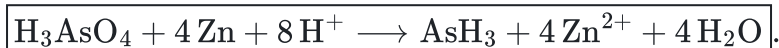
Balancing oxygen with water and hydrogen with hydrogen ions gives



Zinc is oxidized to zinc(II), $[\text{Zn}^{2+}]$:



Multiply this oxidation half-equation by four and add:



Both sides contain one arsenic, four zinc, four oxygen, and eleven hydrogen atoms. Both sides have total charge +8.

F. Degree of protolysis of acetic acid

Acetic acid, $\text{CC}(=\text{O})\text{O}$, dissociates into acetate, $\text{CC}(=\text{O})[\text{O}^-]$, and hydrogen ions:



Let $c_0 = 0.25 \text{ mol dm}^{-3}$, and let x be the concentration dissociated. Neglecting water's contribution to hydrogen-ion concentration,

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-] = x, \quad [\text{CH}_3\text{COOH}] = c_0 - x.$$

Using the usual concentration expression,

$$K_a = \frac{x^2}{c_0 - x}.$$

Solving the quadratic gives

$$x = \frac{-K_a + \sqrt{K_a^2 + 4K_a c_0}}{2} = 2.1123 \times 10^{-3} \text{ mol dm}^{-3}.$$

Thus the fraction dissociated is

$$\alpha = \frac{x}{c_0} = \frac{2.1123 \times 10^{-3}}{0.25} = 0.0084494,$$

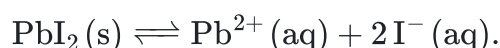
and the percentage is

$$\boxed{100\alpha = 0.84494\% \approx 0.84\%}.$$

Therefore the answer is **c**.

G. Solubility product of lead iodide

Lead(II) iodide, ionic SMILES `[Pb+2].[I-].[I-]`, dissolves according to



The ions are lead(II), `[Pb+2]`, and iodide, `[I-]`. Assuming dissolution is their only source,

$$[\text{Pb}^{2+}] = \frac{[\text{I}^{-}]}{2}.$$

Therefore the concentration-based solubility product is

$$K_{\text{sp},c} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = \frac{[\text{I}^{-}]^3}{2}.$$

Using the concentration actually printed, 2.7 mol dm^{-3} ,

$$K_{\text{sp},c} = \frac{(2.7)^3}{2} = 9.8415 \approx \boxed{9.8 \text{ mol}^3 \text{ dm}^{-9}}.$$

No option matches.

If the intended concentration was $2.7 \times 10^{-3} \text{ mol dm}^{-3}$, then

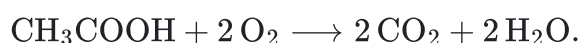
$$K_{\text{sp},c} = \frac{(2.7 \times 10^{-3})^3}{2} = \boxed{9.8 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}},$$

which is option **c**.

The stated solution volume is unnecessary because the ionic concentration is already given. These calculations use the concentration-product convention implicit in the question; a thermodynamic solubility product would instead use activities.

H. Enthalpy of combustion

Complete combustion of acetic acid is



The species are acetic acid `CC(=O)O`, oxygen `O=O`, carbon dioxide `O=C=O`, and water `O`.

By Hess's law,

$$\Delta_c H^\circ = \sum_{\text{products}} \nu \Delta_f H^\circ - \sum_{\text{reactants}} \nu \Delta_f H^\circ.$$

The standard formation enthalpy of elemental oxygen in its standard state is zero. Hence

$$\begin{aligned}\Delta_c H^\circ &= 2(-0.40) + 2(-0.30) - [-0.50 + 2(0)] \\ &= \boxed{-0.90 \text{ MJ mol}^{-1}}.\end{aligned}$$

This is per mole of acetic acid burned, giving option **b**.

I. Equilibrium expression

The reaction is



The molecular species are phosgene (carbonyl dichloride), $\text{O}=\text{C}(\text{Cl})\text{Cl}$; carbon dioxide, $\text{O}=\text{C}=\text{O}$; and chlorine, ClCl . Graphite is an extended solid, whose lattice cannot be represented by a single molecular SMILES.

For a fixed-volume vessel at constant temperature, partial-pressure changes follow the stoichiometric mole changes. Since the equilibrium carbon dioxide pressure is x ,

Gas	Initial partial pressure	Change	Equilibrium partial pressure
COCl_2	a	$-2x$	$a - 2x$
CO_2	0	$+x$	x
Cl_2	0	$+2x$	$2x$

Pure graphite has unit activity and does not appear in the pressure expression. Thus, in the convention of the choices,

$$K_p = \frac{p_{\text{CO}_2}(p_{\text{Cl}_2})^2}{(p_{\text{COCl}_2})^2} = \frac{x(2x)^2}{(a - 2x)^2}.$$

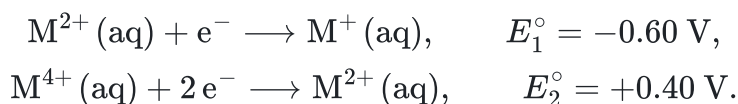
Therefore

$$\boxed{K_p = \frac{4x^3}{(a - 2x)^2}},$$

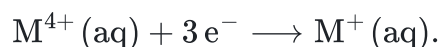
which is option **a**.

K. Combining standard reduction potentials

The given reductions are



Adding them gives



Potentials cannot be added directly. The additive quantities are the standard Gibbs energy changes:

$$\Delta G^\circ = -nFE^\circ.$$

Consequently,

$$-3FE^\circ = -F(-0.60 \text{ V}) - 2F(0.40 \text{ V}),$$

so

$$E^{\circ} = \frac{1(-0.60) + 2(0.40)}{3} \text{ V} = +0.0667 \text{ V}.$$

Thus

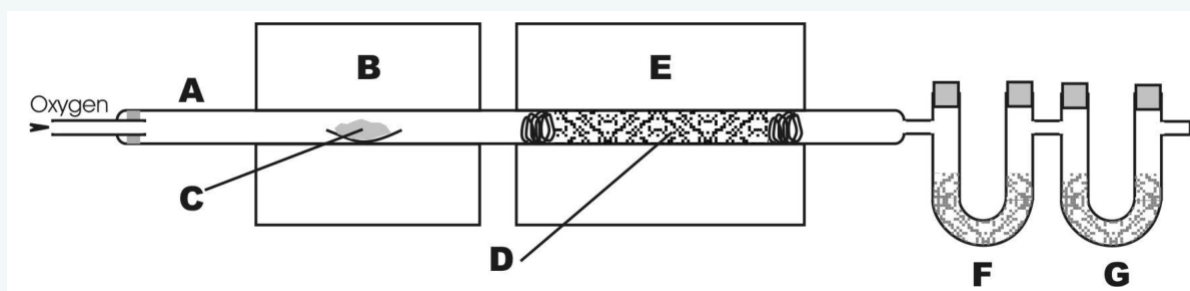
$$E^{\circ} \approx +0.07 \text{ V},$$

giving option **d**.

Because the metal is unspecified, element-specific SMILES cannot be assigned. Generic charged-atom placeholders for the metal(IV), metal(II), and metal(I) ions are [*+4], [*+2], and [*+], respectively; these encode only an unspecified atom and its charge.

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

Problem 2: Liebig combustion analysis and identification of an organic liquid C



Quantitative analysis for carbon and hydrogen was originally carried out using a technique and apparatus (see figure) originally developed in 1831 by the famous chemist Justus Liebig. A carefully weighed sample of organic compound (C) is placed in a combustion tube (A) and vaporized by heating in a furnace (B). The vapours are swept by a stream of oxygen through a heated copper oxide packing (D) and through another furnace (E), which ensures the quantitative oxidation of carbon and hydrogen to carbon dioxide and water. The water vapour is absorbed in a weighed tube (F) containing magnesium perchlorate and the carbon dioxide in another weighed tube (G) containing asbestos impregnated with sodium hydroxide.

A pure liquid sample containing only carbon, hydrogen and oxygen is placed in a 0.57148 g platinum boat, which on reweighing weights 0.61227 g. The sample is ignited and the previously weighed absorption tubes are reweighed. The mass of the water absorption tube has increased from 6.47002 g to 6.50359 g, and the mass of the carbon dioxide tube has increased from 5.46311 g to 5.54466 g.

2.1 Calculate the mass composition of the compound.

2.2 Give the empirical formula of the compound.

To estimate the molar mass of the compound, 1.0045 g was gasified. The volume, measured at a temperature of 350 K and a pressure of 35.0 kPa, was 0.95 dm³.

2.3 Give the molar mass and the molecular formula of the compound.

2.4 Draw possible structures corresponding to the molecular formula excluding cyclic structures, stereo isomers, peroxides and unsaturated compounds. There are about 15 possibilities. Give 10 of them.

When the compound is heated with a sodium hydroxide solution, two products are formed. Fractional distillation of the reaction mixture yields one of the substances. The other substance is purified by distillation after acidification and appears to be an acid.

2.5 What structures are possible for compound C?

0.1005 g of the acid are dissolved in water and titrated with a sodium hydroxide solution with a concentration of $0.1000 \text{ mol dm}^{-3}$. The indicator changes colour on addition of 16.75 cm^3 of hydroxide solution.

2.6 What was the original substance C?

Official English text of the problem.

Answers

- 2.1:** Carbon **54.56%**, hydrogen **9.21%**, oxygen **36.23%** by mass.
- 2.2:** Empirical formula: $\text{C}_2\text{H}_4\text{O}$.
- 2.3:** Molar mass: 88 g mol^{-1} ; molecular formula: $\text{C}_4\text{H}_8\text{O}_2$.
- 2.4:** Ten acceptable constitutional structures are listed below. Stereochemistry is unspecified because stereoisomers are excluded from the count.

Name	Condensed structure	SMILES
Butanoic acid	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OH}$	<chem>CCCC(=O)O</chem>
2-Methylpropanoic acid	$(\text{CH}_3)_2\text{CHC}(=\text{O})\text{OH}$	<chem>CC(C)C(=O)O</chem>
Methyl propanoate	$\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$	<chem>CCC(=O)OC</chem>
Ethyl ethanoate	$\text{CH}_3\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$	<chem>CC(=O)OCC</chem>
Propyl methanoate	$\text{HC}(=\text{O})\text{OCH}_2\text{CH}_2\text{CH}_3$	<chem>CCCOC=O</chem>
Propan-2-yl methanoate	$\text{HC}(=\text{O})\text{OCH}(\text{CH}_3)_2$	<chem>CC(C)OC=O</chem>
2-Hydroxybutanal	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CHO}$	<chem>CCC(O)C=O</chem>
3-Hydroxybutanal	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$	<chem>CC(O)CC=O</chem>
1-Hydroxybutan-2-one	$\text{HOCH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$	<chem>CCC(=O)CO</chem>
3-Hydroxybutan-2-one	$\text{CH}_3\text{C}(=\text{O})\text{CH}(\text{OH})\text{CH}_3$	<chem>CC(=O)C(O)C</chem>

- 2.5:** The four ester candidates are **methyl propanoate** CCC(=O)OC, **ethyl ethanoate** CC(=O)OCC, **propyl methanoate** CCCOC=O, and **propan-2-yl methanoate** CC(C)OC=O.
- 2.6:** The original substance is **ethyl ethanoate (ethyl acetate)**, $\text{CH}_3\text{COOCH}_2\text{CH}_3$, SMILES CC(=O)OCC.

Solution

2.1 — Mass composition

The mass of the sample is

$$m_{\text{sample}} = 0.61227 - 0.57148 = 0.04079 \text{ g.}$$

The absorber mass increases give the amounts of water and carbon dioxide:

$$m(\text{H}_2\text{O}) = 6.50359 - 6.47002 = 0.03357 \text{ g,}$$

$$m(\text{CO}_2) = 5.54466 - 5.46311 = 0.08155 \text{ g.}$$

Using atomic molar masses of 12.01, 1.008, and 16.00 g mol⁻¹ for carbon, hydrogen, and oxygen, respectively,

$$m(\text{C}) = m(\text{CO}_2) \frac{12.01}{44.01} = 0.0222544 \text{ g,}$$

$$m(\text{H}) = m(\text{H}_2\text{O}) \frac{2(1.008)}{18.016} = 0.00375650 \text{ g.}$$

Because the compound contains only carbon, hydrogen, and oxygen, the oxygen mass follows by difference:

$$m(\text{O}) = 0.04079 - 0.0222544 - 0.00375650 = 0.0147791 \text{ g.}$$

Therefore,

$w(\text{C}) = \frac{0.0222544}{0.04079} \times 100\% = 54.56\%,$
$w(\text{H}) = \frac{0.00375650}{0.04079} \times 100\% = 9.21\%,$
$w(\text{O}) = \frac{0.0147791}{0.04079} \times 100\% = 36.23\%.$

2.2 — Empirical formula

The amounts of atoms in the sample are

$$n(\text{C}) = \frac{0.0222544}{12.01} = 1.85299 \times 10^{-3} \text{ mol,}$$

$$n(\text{H}) = \frac{0.00375650}{1.008} = 3.72669 \times 10^{-3} \text{ mol,}$$

$$n(\text{O}) = \frac{0.0147791}{16.00} = 9.23695 \times 10^{-4} \text{ mol.}$$

Dividing by the smallest amount gives

$$n(\text{C}) : n(\text{H}) : n(\text{O}) = 2.006 : 4.035 : 1 \approx 2 : 4 : 1.$$

Thus the empirical formula is



2.3 — Molar mass and molecular formula

Treating the vapour as an ideal gas,

$$pV = nRT, \quad M = \frac{mRT}{pV}.$$

With $R = 8.314 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$,

$$M = \frac{(1.0045 \text{ g})(8.314 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1})(350 \text{ K})}{(35.0 \text{ kPa})(0.95 \text{ dm}^3)} = 87.91 \text{ g mol}^{-1}.$$

The volume has two significant figures, so the reported result is

$$M \approx 88 \text{ g mol}^{-1}.$$

The empirical formula mass is

$$M_{\text{emp}} = 2(12.01) + 4(1.008) + 16.00 = 44.052 \text{ g mol}^{-1}.$$

Hence

$$\frac{M}{M_{\text{emp}}} = \frac{87.91}{44.052} \approx 2,$$

and the molecular formula is



Its complete combustion with oxygen $\text{O}=\text{O}$ is balanced as



2.4 — Ten possible structures

The degree of unsaturation is

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

With rings and carbon–carbon multiple bonds excluded, this requires one carbonyl group. The second oxygen can occur in a carboxylic acid, ester, hydroxyl, or ether group.

The ten structures in the Answers table comprise two carboxylic acids, four esters, two hydroxyaldehydes, and two hydroxyketones. Each has exactly four carbon atoms, eight hydrogen atoms, and two oxygen atoms, with no ring or peroxide bond.

For the requested drawings, the condensed formulas specify the connectivity: every bond is single except the indicated carbonyl double bond. The terminal aldehyde group $-\text{CHO}$ contains a carbonyl carbon bonded to hydrogen. In the hydroxyaldehydes, numbering begins at this aldehyde carbon; in the hydroxyketones, the carbonyl is at carbon 2. No separate stereoisomers are counted.

2.5 — Structures consistent with alkaline hydrolysis

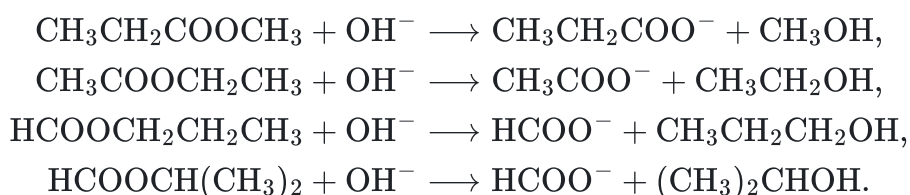
Heating an ester with sodium hydroxide $[\text{Na}^+] \cdot [\text{OH}^-]$ produces an alcohol and a sodium carboxylate. The neutral alcohol can be distilled from the reaction mixture. The carboxylate remains in solution until acidification releases the corresponding carboxylic acid.

For an ester with four carbon atoms, the distribution between the acid and alcohol portions can be $3 + 1$, $2 + 2$, or $1 + 3$. The three-carbon alcohol portion has two possible connectivities. This gives four ester candidates:

Possible compound C	Alcohol obtained	Acid obtained after acidification
Methyl propanoate $\text{CCC}(=\text{O})\text{OC}$	Methanol CO	Propanoic acid $\text{CCC}(=\text{O})\text{O}$
Ethyl ethanoate $\text{CC}(=\text{O})\text{OCC}$	Ethanol CCO	Ethanoic acid $\text{CC}(=\text{O})\text{O}$

Possible compound C	Alcohol obtained	Acid obtained after acidification
Propyl methanoate CCCOC=O	Propan-1-ol CCCO	Methanoic acid O=CO
Propan-2-yl methanoate CC(C)OC=O	Propan-2-ol CC(O)C	Methanoic acid O=CO

The balanced hydrolysis equations, written ionically, are



Here the ions are hydroxide $[\text{OH}^-]$, propanoate $\text{CCC}(=\text{O})[\text{O}^-]$, ethanoate $\text{CC}(=\text{O})[\text{O}^-]$, and methanoate $[\text{O}^-]\text{C}=\text{O}$.

2.6 — Identification of the original substance

All three candidate acids are monocarboxylic and consume one mole of hydroxide per mole of acid. Thus

$$\begin{aligned}
 n_{\text{acid}} &= n_{\text{NaOH}} \\
 &= (0.1000 \text{ mol dm}^{-3})(16.75 \times 10^{-3} \text{ dm}^3) \\
 &= 1.675 \times 10^{-3} \text{ mol}.
 \end{aligned}$$

The acid's experimental molar mass is therefore

$$M_{\text{acid}} = \frac{0.1005 \text{ g}}{1.675 \times 10^{-3} \text{ mol}} = \boxed{60.00 \text{ g mol}^{-1}}.$$

This identifies **ethanoic acid (acetic acid)** $\text{CC}(=\text{O})\text{O}$, whose formula is CH_3COOH and whose formula molar mass is approximately 60.05 g mol^{-1} .

Its titration reaction is

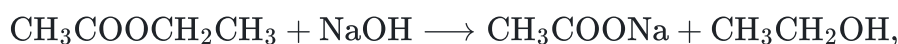


The ethanoate portion contains two carbon atoms, leaving two of the original four carbon atoms for the alcohol portion. That alcohol is therefore ethanol CCO , and the original ester is



with SMILES $\text{CC}(=\text{O})\text{OCC}$.

Its alkaline hydrolysis is



where sodium ethanoate has SMILES $[\text{Na}^+].\text{CC}(=\text{O})[\text{O}^-]$. Ethanol is the first distilled product.

Acidification protonates ethanoate; using hydronium $[\text{OH}_3^+]$ to represent the acidifying solution,



The resulting ethanoic acid is the second isolated product.

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

Problem 3: Analysis of methanol-formaldehyde solutions with dichromate and iodine

In a chemical factory in which formaldehyde is produced by oxidation of methanol, aqueous solutions containing methanol and formaldehyde are to be analyzed. In order to test the method, experiments are first carried out with known amounts of both methanol and formaldehyde. The following aqueous solutions are used:

Methanol, 5.00 g dm^{-3}

Formaldehyde, 5.00 g dm^{-3}

Potassium dichromate, $3.000 \times 10^{-2} \text{ mol dm}^{-3}$

Ammonium iron(II) sulphate, $0.2000 \text{ mol dm}^{-3}$

Iodine, $0.1000 \text{ mol dm}^{-3}$

Sodium thiosulphate, $0.2000 \text{ mol dm}^{-3}$.

I. 10.00 cm^3 methanol solution and 100.00 cm^3 potassium dichromate solution are mixed, approximately 100 cm^3 concentrated sulphuric acid is added and the solution is allowed to stand for about 30 minutes. Excess dichromate ions are then titrated with iron(II) ions with diphenylamine sulphonic acid as a redox indicator (colour change from red-violet to pale green). The volume of the iron(II) solution consumed is 43.5 cm^3 .

II. 10.00 cm^3 of formaldehyde solution and 50.00 cm^3 of iodine solution are mixed. Sodium hydroxide solution is added to alkaline reaction and the mixture is left standing for about 10 minutes. Hydrochloric acid is then added to a neutral reaction, and the excess iodine is determined by titration with thiosulphate, with starch as an indicator. The volume of the thiosulphate solution required is 33.3 cm^3 .

3.1 Using the analysis data in I and II calculate the reacting amounts and the molar ratios of methanol/dichromate ions and formaldehyde/iodine.

3.2 Write balanced equations for all reactions described in experiments I and II.

III. It is checked that iodine does not react with methanol. From a solution containing both methanol and formaldehyde, two 10.00 cm^3 samples are taken.

One sample is mixed with 100.00 cm^3 of potassium dichromate solution and concentrated sulphuric acid as in I. Excess dichromate ions consume 4.8 cm^3 of iron(II) solution.

The other sample is mixed with 50.00 cm^3 of iodine solution and treated as in II. Excess iodine consumes 16.50 cm^3 of thiosulphate solution.

3.3 Give balanced equations for the reactions and calculate the contents of methanol and formaldehyde in the solution. Give your answer in g dm^{-3} .

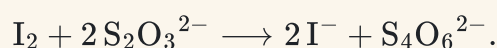
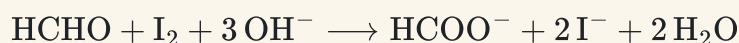
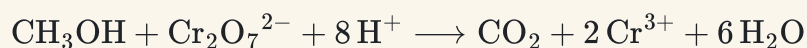
Official English text of the problem.

Answers

- **3.1:** The reacting amounts are:

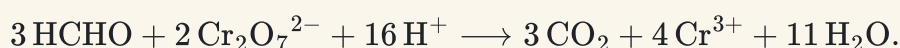
Experiment	Analyte	Oxidant consumed	Analyte/oxidant molar ratio
I	Methanol: 1.56 mmol	Dichromate: 1.550 mmol	1.008 : 1 $\approx$ 1 : 1
II	Formaldehyde: 1.67 mmol	Iodine: 1.670 mmol	0.998 : 1 $\approx$ 1 : 1

- **3.2:** The principal net ionic equations are



Neutralization is $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$. The alkaline iodine transformations are detailed in the solution.

- **3.3:** Formaldehyde also undergoes complete oxidation by acidic dichromate:



The other analytical reactions are those in **3.2**. The concentrations are

Methanol: 1.94 g dm^{-3}

Formaldehyde: 10.1 g dm^{-3} .

Using the rounded molar mass 30.0 g mol^{-1} , the formaldehyde calculation gives 10.05 g dm^{-3} before rounding to three significant figures.

Solution

3.1 — Reacting amounts and molar ratios

Use the rounded molar masses

$$M(\text{CH}_3\text{OH}) = 32.0 \text{ g mol}^{-1}, \quad M(\text{HCHO}) = 30.0 \text{ g mol}^{-1}.$$

Guard digits are retained in intermediate calculations.

In the dichromate back-titration, each dichromate ion accepts six electrons, while each iron(II) ion supplies one. Thus,

$$n(\text{Cr}_2\text{O}_7^{2-})_{\text{remaining}} = \frac{n(\text{Fe}^{2+})}{6}.$$

In the iodine back-titration, one iodine molecule reacts with two thiosulphate ions:

$$n(\text{I}_2)_{\text{remaining}} = \frac{n(\text{S}_2\text{O}_3^{2-})}{2}.$$

Experiment I.

The methanol mass and amount in the sample are

$$m(\text{CH}_3\text{OH}) = (5.00 \text{ g dm}^{-3})(0.01000 \text{ dm}^3) = 0.0500 \text{ g},$$

$$n(\text{CH}_3\text{OH}) = \frac{0.0500}{32.0} = 1.5625 \times 10^{-3} \text{ mol}.$$

The initial dichromate amount is

$$n(\text{Cr}_2\text{O}_7^{2-})_0 = (0.10000)(3.000 \times 10^{-2}) = 3.000 \times 10^{-3} \text{ mol.}$$

The back-titration consumes

$$n(\text{Fe}^{2+}) = (0.0435)(0.2000) = 8.70 \times 10^{-3} \text{ mol.}$$

Consequently,

$$n(\text{Cr}_2\text{O}_7^{2-})_{\text{remaining}} = \frac{8.70 \times 10^{-3}}{6} = 1.450 \times 10^{-3} \text{ mol,}$$

and the amount consumed by methanol is

$$n(\text{Cr}_2\text{O}_7^{2-})_{\text{reacted}} = (3.000 - 1.450) \times 10^{-3} = \boxed{1.550 \times 10^{-3} \text{ mol}}.$$

Therefore,

$$\frac{n(\text{CH}_3\text{OH})}{n(\text{Cr}_2\text{O}_7^{2-})_{\text{reacted}}} = \frac{1.5625}{1.550} = 1.008,$$

identifying the simple stoichiometric ratio

$$\boxed{\text{CH}_3\text{OH} : \text{Cr}_2\text{O}_7^{2-} = 1 : 1}.$$

Experiment II.

The formaldehyde amount is

$$n(\text{HCHO}) = \frac{(5.00)(0.01000)}{30.0} = 1.6667 \times 10^{-3} \text{ mol.}$$

Initially,

$$n(\text{I}_2)_0 = (0.05000)(0.1000) = 5.000 \times 10^{-3} \text{ mol.}$$

Interpreting the printed titration volume as 33.3 cm^3 ,

$$n(\text{S}_2\text{O}_3^{2-}) = (0.0333)(0.2000) = 6.660 \times 10^{-3} \text{ mol.}$$

The iodine remaining is therefore

$$n(\text{I}_2)_{\text{remaining}} = \frac{6.660 \times 10^{-3}}{2} = 3.330 \times 10^{-3} \text{ mol.}$$

Thus,

$$n(\text{I}_2)_{\text{reacted}} = (5.000 - 3.330) \times 10^{-3} = \boxed{1.670 \times 10^{-3} \text{ mol}},$$

and

$$\frac{n(\text{HCHO})}{n(\text{I}_2)_{\text{reacted}}} = \frac{1.6667}{1.670} = 0.998.$$

Hence,

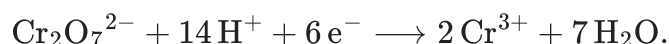
$$\boxed{\text{HCHO} : \text{I}_2 = 1 : 1}.$$

The measured ratios are close to the simple integer ratios; the exact balanced stoichiometries are used below.

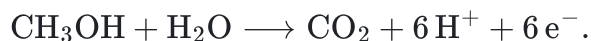
3.2 — Identification of products and balanced reactions

Experiment I: methanol oxidation.

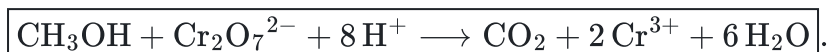
In acidic solution, the dichromate reduction half-reaction is



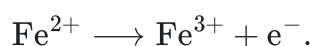
The observed 1 : 1 methanol/dichromate ratio therefore means that one methanol molecule loses six electrons. Its carbon initially has oxidation state -2 , so its final oxidation state is $+4$. Under these acidic conditions the product is carbon dioxide:



Adding the half-reactions gives



For the back-titration, iron(II) is oxidized according to

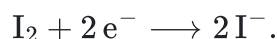


Combining six copies of this half-reaction with dichromate reduction gives



Experiment II: formaldehyde oxidation.

One iodine molecule accepts two electrons:

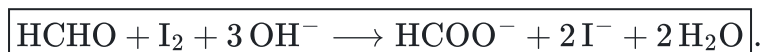


The 1 : 1 formaldehyde/iodine ratio therefore corresponds to a two-electron oxidation of formaldehyde. Its carbon changes from oxidation state 0 to $+2$: the aldehyde group becomes a carboxylate group, giving formate in the alkaline solution.

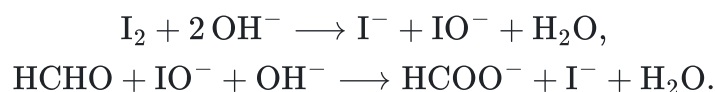
The oxidation half-reaction is



Combining the half-reactions gives



The role of alkaline iodine can also be represented by hypiodite formation followed by oxidation of formaldehyde:



These two equations sum to the same net oxidation equation.

Adding acid neutralizes excess hydroxide,



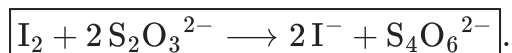
and converts residual hypiodite in the presence of iodide back into iodine:



Finally, thiosulphate is oxidized to tetrathionate:

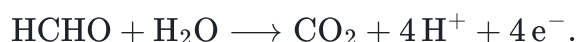


Combining this with iodine reduction gives the titration equation

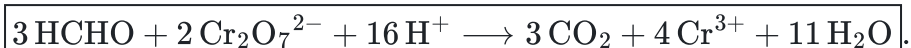


3.3 — Analysis of the mixture

Under the strongly oxidizing conditions of experiment I, formaldehyde is also oxidized completely to carbon dioxide. Its carbon changes from oxidation state 0 to +4, releasing four electrons:



Combining three copies of this half-reaction with two dichromate reduction half-reactions gives



Thus, each mole of methanol consumes one mole of dichromate, while each mole of formaldehyde consumes $2/3$ mole of dichromate. The iodine reaction and both back-titration reactions remain those given in **3.2**.

First determine formaldehyde independently, since iodine does not react with methanol. The iodine remaining after treatment of the second sample is

$$n(\text{I}_2)_{\text{remaining}} = \frac{(0.01650)(0.2000)}{2} = 1.650 \times 10^{-3} \text{ mol}.$$

Therefore, the formaldehyde amount in a 10.00 cm^3 sample is

$$n(\text{HCHO}) = n(\text{I}_2)_{\text{reacted}} = (5.000 - 1.650) \times 10^{-3} = \boxed{3.350 \times 10^{-3} \text{ mol}}.$$

For the first sample, the dichromate remaining is

$$n(\text{Cr}_2\text{O}_7^{2-})_{\text{remaining}} = \frac{(0.0048)(0.2000)}{6} = 1.60 \times 10^{-4} \text{ mol}.$$

Hence the total dichromate consumed is

$$n(\text{Cr}_2\text{O}_7^{2-})_{\text{reacted}} = 3.000 \times 10^{-3} - 1.60 \times 10^{-4} = 2.840 \times 10^{-3} \text{ mol}.$$

Let x be the methanol amount in either original 10.00 cm^3 sample. The dichromate balance is

$$x + \frac{2}{3}n(\text{HCHO}) = n(\text{Cr}_2\text{O}_7^{2-})_{\text{reacted}}.$$

Thus,

$$x = 2.840 \times 10^{-3} - \frac{2}{3}(3.350 \times 10^{-3}) = \boxed{6.0667 \times 10^{-4} \text{ mol}}.$$

The requested mass concentrations refer to the original sample volume, 0.01000 dm^3 :

$$\rho(\text{CH}_3\text{OH}) = \frac{(6.0667 \times 10^{-4})(32.0)}{0.01000} = 1.9413 \text{ g dm}^{-3} \approx \boxed{1.94 \text{ g dm}^{-3}},$$

$$\rho(\text{HCHO}) = \frac{(3.350 \times 10^{-3})(30.0)}{0.01000} = 10.05 \text{ g dm}^{-3} \approx \boxed{10.1 \text{ g dm}^{-3}}.$$

Names and SMILES for the species used

Species	SMILES
Methanol, CH_3OH	<chem>CO</chem>
Formaldehyde (methanal), HCHO	<chem>C=O</chem>
Carbon dioxide, CO_2	<chem>O=C=O</chem>

Species	SMILES
Formate (methanoate) ion, HCOO^-	<chem>[H]C(=O)[O-]</chem>
Dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$	<chem>[O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-]</chem>
Chromium(III) ion, Cr^{3+}	<chem>[Cr+3]</chem>
Iron(II) ion, Fe^{2+}	<chem>[Fe+2]</chem>
Iron(III) ion, Fe^{3+}	<chem>[Fe+3]</chem>
Iodine, I_2	<chem>I I</chem>
Iodide ion, I^-	<chem>[I-]</chem>
Hypoiodite ion, IO^-	<chem>[O-]I</chem>
Thiosulphate ion, $\text{S}_2\text{O}_3^{2-}$	<chem>[O-]S(=O)(=O)[S-]</chem>
Tetrathionate ion, $\text{S}_4\text{O}_6^{2-}$	<chem>[O-]S(=O)(=O)SSS(=O)(=O)[O-]</chem>
Hydrogen ion, H^+	<chem>[H+]</chem>
Hydroxide ion, OH^-	<chem>[OH-]</chem>
Water, H_2O	<chem>O</chem>

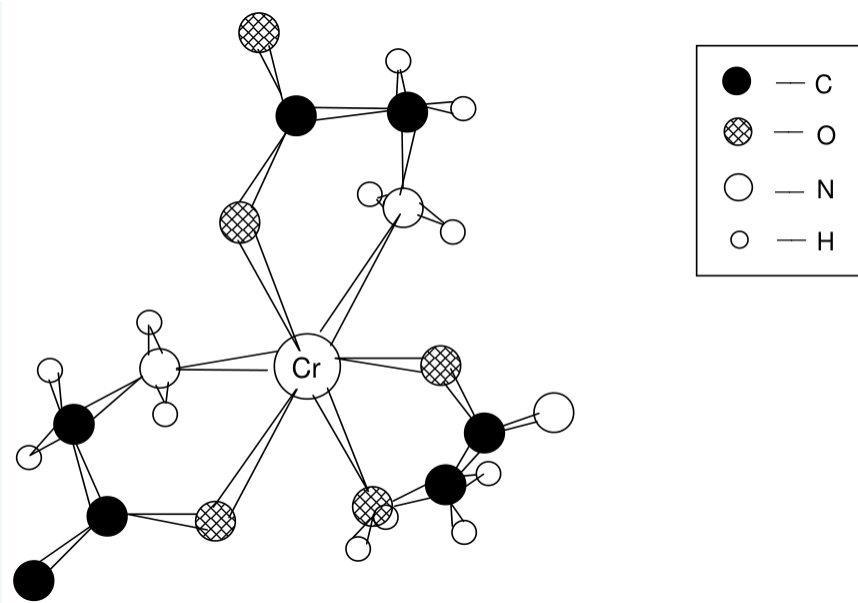
These SMILES specify connectivity and formal charges; aqueous solvation is implicit. Dichromate consists of two approximately tetrahedral chromium–oxygen units sharing one oxygen, a geometry not explicitly encoded by its SMILES. Electron transfers are expressed by the half-reactions above.

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

Problem 4: Coordination compounds of chromium(III): glycinate complex isomers and a chromium chloride hydrate

A transition metal atom or ion may be directly bonded to a number of atoms or molecules that surround it (ligands), forming a characteristic pattern. This is the essential structural feature of an important class of so-called coordination or complex compounds. If two or more atoms from one individual ligand form bonds to the same central atom then the ligand is said to form a chelate (Greek chele = crab' claw).

The glycinate ion, $\text{NH}_2\text{—CH}_2\text{—COO}^-$, is a bidentate chelate ligand which can form, for instance, tris-glycinato-chromium(III) complexes. The figure shows one possible structure of such a complex. Oxygen and nitrogen are forced to coordinate to adjacent octahedral positions, as the N—C—C—O chain is too short to "embrace" the chromium ion.



4.1 How many different configurational isomers of the complex are possible, not counting optical isomers?

4.2 Which of these isomers can be further resolved into optical isomers?

Another coordination compound of chromium was analyzed and found to have the following mass composition: 19.5 % Cr, 40.0 % Cl, 4.5 % H, and 36.0 % O. A 0.533 g sample of the compound was dissolved in 100 cm³ of water, and 10 cm³ of nitric acid (2 mol dm⁻³) was added. Excess of silver nitrate solution was then added and the precipitate formed was then filtered, washed, dried and weighed. Its mass was found to be 0.287 g.

When a 1.06 g sample was gently heated to 100 °C in a stream of dry air, 0.144 g of water was driven off.

The freezing point of a solution prepared from 1.33 g of the compound and 100 cm³ of water, was found to be -0.18 °C. (Molar freezing point depression of water is 1.82 K kg mol⁻¹).

Use all the experimental information to solve the following problems:

4.3 Derive the empirical formula of the compound.

4.4 Deduce formula for the compound showing the ligands of the chromium ion. Give molar ratios to support your result.

4.5 Sketch all possible steric arrangements of the ligands about the chromium ion.

Official English text of the problem.

Answers

- 4.1:** Two geometrical isomers: **fac** and **mer** tris(glycinato)chromium(III).
- 4.2:** Both have an enantiomeric pair, conventionally designated Δ and Λ . Thus there are **four configurational stereoisomers** altogether.
- 4.3:** $\text{CrCl}_3\text{H}_{12}\text{O}_6$, conventionally written $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, chromium(III) chloride hexahydrate.

- **4.4:** $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$, **tetraaquadichloridochromium(III) chloride dihydrate**.

Per chromium there are two coordinated chloride ions, four coordinated waters, one chloride counterion, and two waters of crystallization.

- **4.5:** **cis** and **trans** arrangements of $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$; both are achiral.

Names, structural SMILES, and precise descriptions of the arrangements follow.

Solution

The coordination structures below use **extended SMILES**, with dative-bond arrows pointing toward the metal and @OH tags specifying octahedral stereochemistry. These specify connectivity and configuration, but do not fix chelate-ring conformations or crystal packing.

4.1 — Geometrical isomers of the glycinate complex

Glycinate, or 2-aminoacetate, $\text{NH}_2\text{CH}_2\text{COO}^-$, has SMILES NCC(=O)[O-]. Each ligand binds the chromium(III) ion, Cr^{3+} , SMILES [Cr+3], through its nitrogen and one carboxylate oxygen at adjacent octahedral positions.

The three nitrogen donors can occupy only two distinct types of arrangement:

Isomer	Arrangement of the nitrogen donors	Trans donor pairs
fac-tris(glycinato)chromium(III)	All three occupy one triangular face; every nitrogen pair is cis.	Three nitrogen–oxygen pairs
mer-tris(glycinato)chromium(III)	Two are opposite; the three lie in a plane through chromium.	One nitrogen–nitrogen, one oxygen–oxygen, and one nitrogen–oxygen pair

Three nitrogen donors can contain either zero or one trans pair. Accounting for the connections within each chelate gives no further geometrical class when mirror images are counted together.

Therefore, the answer is **two**.

4.2 — Optical isomerism

In both geometrical isomers, the three chelate rings form a handed arrangement around chromium. Reflection reverses this handedness, and no rotation superimposes the resulting structures while preserving the three nitrogen–oxygen chelate connections.

Thus **both fac and mer forms occur as Δ/Λ enantiomeric pairs**. The mer donor positions alone must not be used to judge chirality: which nitrogen is connected to which oxygen also matters.

The following SMILES give both members of each pair; “first” and “mirror” do not assign an absolute Δ/Λ label.

Tris(glycinato)chromium(III) configuration	Extended stereochemical SMILES
fac, first enantiomer	<chem>[Cr@OH15+3]123(<- [NH2]CC(=O)[O-]->1)(<- [NH2]CC(=O)[O-]->2)<- [NH2]CC(=O)[O-]->3</chem>

Tris(glycinato)chromium(III) configuration	Extended stereochemical SMILES
fac, mirror image	<chem>[Cr@OH5+3]123(<-[NH2]CC(=O)[O-]->1)(<-[NH2]CC(=O)[O-]->2)<-[NH2]CC(=O)[O-]->3</chem>
mer, first enantiomer	<chem>[Cr@OH8+3]123(<-[NH2]CC(=O)[O-]->1)(<-[NH2]CC(=O)[O-]->2)<-[NH2]CC(=O)[O-]->3</chem>
mer, mirror image	<chem>[Cr@OH10+3]123(<-[NH2]CC(=O)[O-]->1)(<-[NH2]CC(=O)[O-]->2)<-[NH2]CC(=O)[O-]->3</chem>

There are therefore $2 \times 2 = \boxed{4}$ configurational stereoisomers, excluding differences in ring conformation.

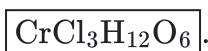
4.3 — Empirical formula

Use the rounded atomic molar masses 52.0, 35.5, 1.0, 16.0, 108.0 g mol⁻¹ for Cr, Cl, H, O, and Ag, respectively.

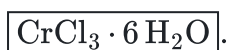
For a 100 g sample:

Element	Amount / mol	Ratio relative to chromium
Cr	19.5/52.0 = 0.375	1
Cl	40.0/35.5 = 1.127	3.00
H	4.5/1.0 = 4.5	12
O	36.0/16.0 = 2.25	6.00

Hence the empirical formula is



The hydrogen and oxygen correspond to six molecules of water, H₂O, SMILES o, per chromium:

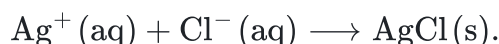


This composition alone does not distinguish coordinated water from water of crystallization. Its formula molar mass is

$$M = 52.0 + 3(35.5) + 6(18.0) = \boxed{266.5 \text{ g mol}^{-1}}.$$

4.4 — Coordination formula

Chloride precipitation. The precipitate is silver(I) chloride, AgCl, with ionic formula-unit SMILES [Ag+].[Cl-]. Silver(I) ions, [Ag+], precipitate free chloride ions, [Cl-]:



The amount precipitated is

$$n(\text{AgCl}) = \frac{0.287 \text{ g}}{143.5 \text{ g mol}^{-1}} = 2.00 \times 10^{-3} \text{ mol}.$$

The sample contains

$$n(\text{formula units}) = \frac{0.533 \text{ g}}{266.5 \text{ g mol}^{-1}} = 2.00 \times 10^{-3} \text{ mol}.$$

Consequently,

$$\frac{n(\text{precipitable chloride})}{n(\text{Cr})} = 1.00.$$

Under the intended precipitation conditions, this measures chloride outside the coordination sphere. Therefore, **one of the three chlorides is a counterion, and two are coordinated.**

Water lost on heating. Interpreting the printed "0.144" as 0.144 g,

$$n(\text{water lost}) = \frac{0.144 \text{ g}}{18.0 \text{ g mol}^{-1}} = 8.00 \times 10^{-3} \text{ mol},$$

whereas

$$n(\text{formula units}) = \frac{1.06 \text{ g}}{266.5 \text{ g mol}^{-1}} = 3.98 \times 10^{-3} \text{ mol}.$$

Thus

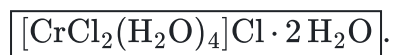
$$\frac{n(\text{water lost})}{n(\text{Cr})} = 2.01 \simeq 2.$$

Gentle heating therefore removes **two waters of crystallization** per chromium. Of the six waters in total, **four remain as aqua ligands.**

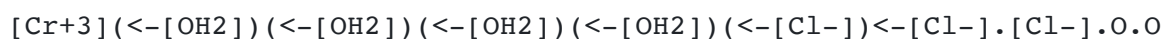
The resulting octahedral coordination sphere contains four aqua ligands and two chlorido ligands. Its charge is

$$+3 + 2(-1) + 4(0) = +1.$$

The compound is therefore **tetraaquadichloridochromium(III) chloride dihydrate:**



Its extended SMILES, leaving cis/trans geometry unspecified, is:



The corresponding loss of lattice water is



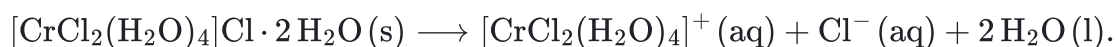
Freezing-point confirmation. Taking 100 cm³ of water as 0.100 kg, the analytical molality is

$$m = \frac{1.33/266.5 \text{ mol}}{0.100 \text{ kg}} = 4.99 \times 10^{-2} \text{ mol kg}^{-1}.$$

Using $\Delta T_f = iK_fm$,

$$i = \frac{0.18 \text{ K}}{(1.82 \text{ K kg mol}^{-1})(4.99 \times 10^{-2} \text{ mol kg}^{-1})} = 1.98 \simeq 2.$$

Thus each formula unit produces approximately **two dissolved solute particles**, consistent with



These particles are the **tetraaquadichloridochromium(III) cation** and the **chloride counterion**. The lattice water joins the solvent.

All three experimental ratios agree:

$$\frac{n(\text{free chloride})}{n(\text{Cr})} = 1.00, \quad \frac{n(\text{lattice water})}{n(\text{Cr})} = 2.01, \quad \frac{n(\text{solute particles})}{n(\text{Cr})} = 1.98.$$

4.5 — All ligand arrangements

For an octahedral complex with four identical aqua ligands and two identical chlorido ligands, the chlorido ligands can be either **adjacent** or **opposite**.

To describe the required sketches precisely, place chromium at the origin and the six donor atoms along $+x, -x, +y, -y, +z, -z$.

Cation	Precise spatial arrangement	Extended stereochemical SMILES
cis-tetraaquadichloridochromium(III)	Chlorido ligands at $+y$ and $+z$, making a 90° angle. Aqua ligands occupy $+x, -x, -y, -z$.	<chem>[Cr@OH25+3](<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[Cl-])<-[Cl-]</chem>
trans-tetraaquadichloridochromium(III)	Chlorido ligands at $+z$ and $-z$, making a 180° angle. Aqua ligands occupy $+x, -x, +y, -y$.	<chem>[Cr@OH27+3](<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[Cl-])<-[Cl-]</chem>

Both arrangements possess mirror symmetry and are **achiral**. The analytical data do not distinguish which of these two geometrical isomers was present.

The solution was checked against the official solution.

Problem 5: Solubility of iodine in potassium iodide solutions

Iodine is soluble to a certain extent in pure water. It is, however, more soluble in solutions containing iodide ions. By studying the total solubility of iodine as a function of iodide concentration, the equilibrium constants of the following reactions can be determined:

Equation	Equilibrium constants
$\text{I}_2(\text{s}) \rightleftharpoons \text{I}_2(\text{aq})$	k_1 (1)
$\text{I}_2(\text{s}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$	k_2 (2)
$\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$	k_3 (3)

5.1 Give the equilibrium equations for (1) – (3).

Solutions of known potassium iodide concentration $[\text{I}^-]_{\text{tot}}$ were equilibrated with solid iodine. Subsequent titration with sodium thiosulphate solution served to determine the total solubility of iodine $[\text{I}_2]_{\text{tot}}$.

The experiments yielded the following results:

$[\text{I}^-]_{\text{tot}} / \text{mmol dm}^{-3}$	10.00	20.00	30.00	40.00	50.00
$[\text{I}_2]_{\text{tot}} / \text{mmol dm}^{-3}$	5.85	10.53	15.11	19.96	24.82

5.2 Plot $[I_2]_{\text{tot}}$ versus $[I^-]_{\text{tot}}$ in a diagram.

5.3 Derive a suitable algebraic expression relating $[I_2]_{\text{tot}}$ and $[I^-]_{\text{tot}}$.

5.4 Use the graph to determine values of the equilibrium constants k_1 , k_2 , and k_3 .

Official English text of the problem.

Answers

- 5.1 Using concentration equilibrium constants,

$$k_1 = [I_2], \quad k_2 = \frac{[I_3^-]}{[I^-]}, \quad k_3 = \frac{[I_3^-]}{[I_2][I^-]}$$

and $k_2 = k_1 k_3$.

- 5.2 The points lie approximately on a straight line, with $[I^-]_{\text{tot}}$ on the horizontal axis and $[I_2]_{\text{tot}}$ on the vertical axis:

$$[I_2]_{\text{tot}} \simeq 1.043 \text{ mmol dm}^{-3} + 0.4737 [I^-]_{\text{tot}}.$$

- 5.3

$$[I_2]_{\text{tot}} = k_1 + \frac{k_2}{1 + k_2} [I^-]_{\text{tot}} = k_1 + \frac{k_1 k_3}{1 + k_1 k_3} [I^-]_{\text{tot}}.$$

- 5.4 From the fitted line,

$$k_1 \approx 1.04 \times 10^{-3} \text{ mol dm}^{-3}, \quad k_2 \approx 0.900, \quad k_3 \approx 8.63 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}.$$

These are approximate graphical determinations.

Solution

The molecular and ionic species used below are:

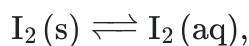
Species	Formula	SMILES
Iodine	I_2	<chem>II</chem>
Iodide ion	I^-	<chem>[I-]</chem>
Triiodide ion	I_3^-	<chem>I[I-]I</chem>
Thiosulphate ion	$S_2O_3^{2-}$	<chem>[O-]S(=O)(=O)[S-]</chem>
Tetrathionate ion	$S_4O_6^{2-}$	<chem>[O-]S(=O)(=O)SSS(=O)(=O)[O-]</chem>

Triiodide is linear. Its SMILES gives formal connectivity; it does not convey the three-centre, four-electron bonding or the distribution of charge.

5.1 — Equilibrium expressions

Use the concentration convention implied by the problem, treating the solutions as ideal. The activity of pure solid iodine is unity, so the solid does not appear in the equilibrium expressions. Unsubscripted concentrations below denote free aqueous species.

For reaction (1),

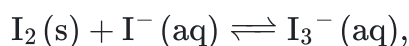


hence

$$k_1 = [\text{I}_2].$$

Thus the concentration of free molecular iodine remains constant while the solution is equilibrated with solid iodine.

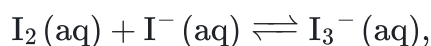
For reaction (2),



hence

$$k_2 = \frac{[\text{I}_3^-]}{[\text{I}^-]}.$$

For reaction (3),



hence

$$k_3 = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}.$$

Adding reactions (1) and (3) gives reaction (2), so their constants satisfy

$$k_2 = k_1 k_3.$$

With concentrations in mol dm^{-3} , these concentration constants have units mol dm^{-3} , no units, and $\text{dm}^3 \text{mol}^{-1}$, respectively.

5.2 — Description of the graph

Interpret the second row of numerical data as $[\text{I}_2]_{\text{tot}}$, consistently with the experimental description.

Draw the horizontal axis as $[\text{I}^-]_{\text{tot}}$, from 0 to 50 mmol dm^{-3} , and the vertical axis as $[\text{I}_2]_{\text{tot}}$, from 0 to about 26 mmol dm^{-3} . Plot the five points, with both coordinates in mmol dm^{-3} :

$$(10.00, 5.85), \quad (20.00, 10.53), \quad (30.00, 15.11), \quad (40.00, 19.96), \quad (50.00, 24.82).$$

Draw a straight best-fit line through the group of points and extend it to the vertical axis.

For a numerical check, let x and y be the numerical concentrations in mmol dm^{-3} . Then

$$\bar{x} = 30.00, \quad \bar{y} = 15.254,$$

and the least-squares slope is

$$m = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sum_i (x_i - \bar{x})^2} = \frac{473.7}{1000} = 0.4737.$$

The intercept is

$$b = \bar{y} - m\bar{x} = 15.254 - 0.4737(30.00) = 1.043.$$

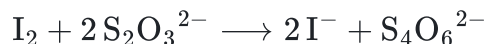
Thus the line crosses the vertical axis at $1.043 \text{ mmol dm}^{-3}$ and passes through approximately $(50.00, 24.73)$.

5.3 — Relation between the total concentrations

Each triiodide ion forms from one iodine molecule and one iodide ion. The analytical iodide balance is therefore

$$[\text{I}^-]_{\text{tot}} = [\text{I}^-] + [\text{I}_3^-].$$

The iodine titration measures iodine equivalents. The balanced titration reactions are



and



One mole of either iodine or triiodide consumes two moles of thiosulphate. Consequently, each mole of triiodide contributes one mole to the measured total iodine solubility:

$$[\text{I}_2]_{\text{tot}} = [\text{I}_2] + [\text{I}_3^-].$$

From reaction (2),

$$[\text{I}_3^-] = k_2[\text{I}^-].$$

Substitution into the iodide balance gives

$$[\text{I}^-]_{\text{tot}} = (1 + k_2)[\text{I}^-],$$

so

$$[\text{I}_3^-] = \frac{k_2}{1 + k_2} [\text{I}^-]_{\text{tot}}.$$

Since $[\text{I}_2] = k_1$,

$$[\text{I}_2]_{\text{tot}} = k_1 + \frac{k_2}{1 + k_2} [\text{I}^-]_{\text{tot}}.$$

Using $k_2 = k_1 k_3$, the equivalent expression is

$$[\text{I}_2]_{\text{tot}} = k_1 + \frac{k_1 k_3}{1 + k_1 k_3} [\text{I}^-]_{\text{tot}}.$$

This explains the observed straight line: its intercept is k_1 , and its slope is $k_2/(1 + k_2)$.

5.4 — Determination of the equilibrium constants

The intercept gives

$$k_1 = 1.043 \text{ mmol dm}^{-3} = 1.043 \times 10^{-3} \text{ mol dm}^{-3},$$

or approximately

$$k_1 \approx 1.04 \times 10^{-3} \text{ mol dm}^{-3}.$$

From the slope,

$$m = \frac{k_2}{1 + k_2} \implies k_2 = \frac{m}{1 - m}.$$

Therefore,

$$k_2 = \frac{0.4737}{1 - 0.4737} = \frac{0.4737}{0.5263} = 0.900057 \dots,$$

giving

$$k_2 \approx 0.900.$$

Finally,

$$k_3 = \frac{k_2}{k_1} = \frac{0.900057\dots}{1.043 \times 10^{-3} \text{ mol dm}^{-3}},$$

so

$$k_3 \approx 8.63 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}.$$

The solution was checked against the official solution.

Problem 6: Identification of organic compounds A-D from analytical data

A white solid organic acid, **A**, contains only carbon, hydrogen and oxygen. To obtain an approximate value for the molar mass, 10.0 g of the acid were dissolved in water. Crushed ice was added and vigorous shaking caused a decrease in temperature to -2.5°C . The ice was quickly removed. The mass of the solution was 76.1 g, and its pH value was determined to be 1.4. In a handbook the molar freezing point depression constant for water was found to be $1.86 \text{ K kg mol}^{-1}$. A more precise determination of the molar mass of the acid was then carried out. 0.120 g of the acid was titrated with a sodium hydroxide solution with a concentration of $0.100 \text{ mol dm}^{-3}$. Phenolphthalein was used as an indicator, and when 23.4 cm^3 of hydroxide solution was added the indicator turned red.

6.1 Give the molar mass and the structure of acid **A**.

Liquid **B** dissolves in water up to 10 %. The pH value of the solution is about 4. **B** is not easily oxidized, but following the iodoform reaction and subsequent acidification it is oxidized to acid **A**. 0.10 g of **B** consumes 1.5 g of iodine.

When **B** reacts with sodium, hydrogen is evolved and a metal organic compound is formed. The molar mass of **B** is approximately 100 g mol^{-1} .

6.2 Write the chemical equation for the iodoform reaction and for the reaction with sodium. For the organic molecules structural formulas should be used.

Compound **C** in aqueous solution has a conductivity which differs very little from that of pure water. Alkaline hydrolysis of **C** yields ammonia. 0.120 g of **C** was treated with hot, dilute sodium hydroxide solution and the gas formed was led into 50.0 cm^3 hydrochloric acid with a concentration of $0.100 \text{ mol dm}^{-3}$. The excess acid was titrated with 10.0 cm^3 sodium hydroxide solution with a concentration of $0.100 \text{ mol dm}^{-3}$.

Acid hydrolysis of **C** yields carbon dioxide. From the freezing point depression, the molar mass of **C** is estimated to be between 40 g mol^{-1} and 70 g mol^{-1} .

6.3 Give the structure of **C**. Write reaction equations for both the alkaline and the acid hydrolysis.

If **C** is allowed to react with the ethyl ester of acid **A** in the presence of a strong alkaline catalyst, ethanol and compound **D** are formed. The composition of **D** is 37.5 % C, 3.1 % H, 21.9 % N, and the remainder is oxygen. The compound is an acid.

6.4 Give the structure for **D**. Which is the "acid" hydrogen atom? Mark it with * in the structure.

Official English text of the problem.

Answers

- 6.1: A is malonic acid (propanedioic acid)**, $\text{O}=\text{C}(\text{O})\text{CC}(=\text{O})\text{O}$, with structure $\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$. The titration gives $M = 103 \text{ g mol}^{-1}$; its formula mass is approximately 104 g mol^{-1} .
- 6.2: B is acetylacetone (pentane-2,4-dione)**, $\text{CC}(=\text{O})\text{CC}(\text{C})=\text{O}$. Its balanced reactions, written in ionic form, are:

$$\text{CH}_3-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3 + 6 \text{I}_2 + 8 \text{OH}^- \longrightarrow [\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{O}]^{2-} + 2 \text{H}-\text{C}(\text{I})(\text{I})-\text{I} + 6 \text{I}^- + 6 \text{H}_2\text{O}$$
 followed by

$$[\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{O}]^{2-} + 2 \text{H}^+ \longrightarrow \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{OH}.$$
 With sodium:

$$2 \text{CH}_3-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3 + 2 \text{Na} \longrightarrow 2 \text{Na}^+ + 2 [\text{CH}_3-\text{C}(=\text{O})-\text{CH}-\text{C}(=\text{O})-\text{CH}_3]^- + \text{H}_2.$$
 In the last equation, the organic anion is shown using its central-carbon anionic resonance contributor.
- 6.3: C is urea**, $\text{NC}(=\text{O})\text{N}$, $M = 60.0 \text{ g mol}^{-1}$:

$$\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2 + 2 \text{OH}^- \longrightarrow \text{CO}_3^{2-} + 2 \text{NH}_3$$

$$\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2 + \text{H}_2\text{O} + 2 \text{H}^+ \longrightarrow \text{CO}_2 + 2 \text{NH}_4^+.$$
- 6.4: D is barbituric acid (malonylurea)**, $\text{O}=\text{C}1\text{CC}(=\text{O})\text{NC}(=\text{O})\text{N}1$, with formula $\text{C}_4\text{H}_4\text{N}_2\text{O}_3$. Mark either hydrogen on the **C5 methylene carbon**, between two carbonyl groups, with an asterisk. A precise ring description is

$$-\text{NH}-\text{C}(=\text{O})-\text{NH}-\text{C}(=\text{O})-\text{C}(\text{H})(\text{H}^*)-\text{C}(=\text{O})-,$$
 with the final carbonyl carbon bonded back to the first nitrogen. The two methylene hydrogens are equivalent before deprotonation.

Solution

6.1 — Identification and molar mass of A

The mass of water remaining in the solution is

$$m_{\text{water}} = 76.1 - 10.0 = 66.1 \text{ g} = 0.0661 \text{ kg}.$$

First neglect acid dissociation in the explicitly approximate freezing-point determination:

$$\Delta T_f = K_f b.$$

Thus

$$b = \frac{2.5}{1.86} = 1.34 \text{ mol kg}^{-1},$$

and the apparent amount of acid is

$$n_{\text{app}} = (1.34 \text{ mol kg}^{-1})(0.0661 \text{ kg}) = 0.0888 \text{ mol}.$$

Consequently,

$$M_{\text{app}} = \frac{10.0 \text{ g}}{0.0888 \text{ mol}} = 112.6 \text{ g mol}^{-1} \approx 1.1 \times 10^2 \text{ g mol}^{-1}.$$

The pH corresponds, approximately, to

$$[\text{H}^+] \approx 10^{-1.4} = 4.0 \times 10^{-2} \text{ mol dm}^{-3}.$$

The acid concentration is of order 1 mol dm^{-3} , so dissociation contributes only a modest fraction of the dissolved particles. Neglecting it is suitable for estimating the number of titratable protons, although an exact correction cannot be calculated from the supplied information.

The amount of hydroxide consumed in the titration is

$$n(\text{OH}^-) = (0.100 \text{ mol dm}^{-3})(23.4 \times 10^{-3} \text{ dm}^3) = 2.34 \times 10^{-3} \text{ mol}.$$

If each acid molecule consumes z hydroxide ions, its molar mass is

$$M = z \frac{0.120}{2.34 \times 10^{-3}} = z(51.3) \text{ g mol}^{-1}.$$

Comparison with the cryoscopic estimate gives

$$z \approx \frac{112.6}{51.3} \approx 2.2.$$

The appropriate integer is therefore **two**: A is dibasic.

The more precise experimental molar mass is consequently

$$M(A) = \frac{2(0.120)}{2.34 \times 10^{-3}} = 102.6 \text{ g mol}^{-1} \approx 103 \text{ g mol}^{-1}.$$

This identifies **malonic acid**, $\text{O}=\text{C}(\text{O})\text{CC}(=\text{O})\text{O}$:



Its formula, $\text{C}_3\text{H}_4\text{O}_4$, gives approximately 104 g mol^{-1} . Its identification is also confirmed by the reactions of B.

The neutralization is



The organic product is the **malonate dianion**, $\text{O}=\text{C}([\text{O}^-])\text{CC}(=\text{O})[\text{O}^-]$.

6.2 — Identification and reactions of B

Using $M(\text{I}_2) \approx 254 \text{ g mol}^{-1}$,

$$n(\text{I}_2) = \frac{1.5}{254} = 5.9 \times 10^{-3} \text{ mol}.$$

The approximate amount of B is

$$n(B) \approx \frac{0.10}{100} = 1.0 \times 10^{-3} \text{ mol.}$$

Hence

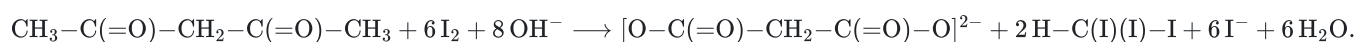
$$\frac{n(I_2)}{n(B)} \approx 5.9 \approx 6.$$

A methyl ketone group consumes three iodine molecules in the iodoform reaction. Six iodine molecules per molecule of B therefore indicate **two methyl ketone groups**. Replacing both methyl ketone ends by carboxyl groups must give malonic acid, so B is



acetylacetone, $\text{CC}(=\text{O})\text{CC}(\text{C})=\text{O}$. Its formula $\text{C}_5\text{H}_8\text{O}_2$ has molar mass approximately 100 g mol^{-1} , as required.

The double iodoform reaction is



The organic products are malonate and **iodoform (triiodomethane)**, $\text{IC}(\text{I})\text{I}$. Acidification protonates malonate:

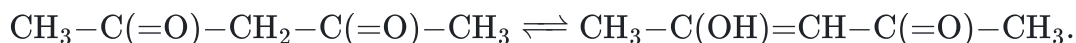


The predicted iodine consumption is

$$m(\text{I}_2) = \frac{0.10}{100} \times 6 \times 254 = 1.52 \text{ g},$$

which agrees with the reported 1.5 g.

The diketone structure explains resistance to ordinary mild oxidation. Its acidity and reaction with sodium arise from the hydrogens between its two carbonyl groups and from keto–enol tautomerism:



The enol is **4-hydroxypent-3-en-2-one**, $\text{CC}(\text{O})=\text{CC}(\text{C})=\text{O}$; specifying its alkene geometry is unnecessary for these reactions.

Sodium replaces one acidic hydrogen per molecule:



The salt is **sodium acetylacetonate**, $[\text{Na}^+].[\text{CH}_3-\text{C}(=\text{O})-\text{CH}-\text{C}(=\text{O})-\text{CH}_3]^-$. Its **acetylacetonate anion**, $[\text{CH}_3-\text{C}(=\text{O})-\text{CH}-\text{C}(=\text{O})-\text{CH}_3]^-$, has charge delocalized over the central carbon and both oxygen atoms. The displayed structure and SMILES represent one resonance contributor, rather than this delocalization.

6.3 — Identification and hydrolysis of C

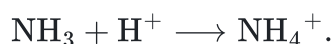
The hydrochloric acid initially contains

$$n_0(\text{H}^+) = (50.0 \times 10^{-3})(0.100) = 5.00 \times 10^{-3} \text{ mol.}$$

The excess acid contains

$$n_{\text{excess}}(\text{H}^+) = (10.0 \times 10^{-3})(0.100) = 1.00 \times 10^{-3} \text{ mol.}$$

Ammonia absorbs one proton per molecule:



Therefore,

$$n(\text{NH}_3) = 5.00 \times 10^{-3} - 1.00 \times 10^{-3} = 4.00 \times 10^{-3} \text{ mol.}$$

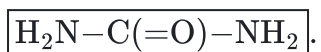
If one mole of C yields r moles of ammonia,

$$M(C) = \frac{0.120 r}{4.00 \times 10^{-3}} = 30.0r \text{ g mol}^{-1}.$$

The stated range $40\text{--}70 \text{ g mol}^{-1}$ permits only $r = 2$, giving

$$M(C) = 60.0 \text{ g mol}^{-1}.$$

A neutral compound of this mass that yields two ammonia molecules on alkaline hydrolysis and carbon dioxide on acid hydrolysis is **urea**, $\text{NC}(=\text{O})\text{N}$:

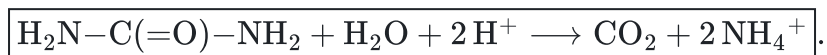


Its neutral molecular structure is consistent with the very low conductivity.

In alkaline solution, the carbon-containing product is carbonate:



In acidic solution, the nitrogen-containing product remains protonated as ammonium:



6.4 — Identification of D and its acidic hydrogen

The oxygen percentage is

$$100.0 - 37.5 - 3.1 - 21.9 = 37.5\%.$$

Using ordinary rounded atomic masses, the atomic ratio is

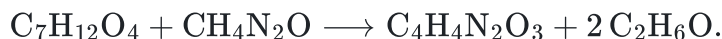
$$\frac{37.5}{12} : \frac{3.1}{1} : \frac{21.9}{14} : \frac{37.5}{16} \approx 4 : 4 : 2 : 3.$$

Thus the empirical formula is



The ester is **diethyl malonate**, $\text{CCOC}(=\text{O})\text{CC}(=\text{O})\text{OCC}$. Each of its two ester groups can react with one amino group of urea, eliminating a molecule of **ethanol**, CCO . Joining both ends produces a six-membered ring.

The formal condensation balance is



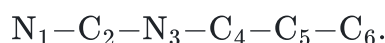
Consequently, the molecular formula equals the empirical formula, and D is **barbituric acid**, $\text{O}=\text{C}_1\text{CC}(=\text{O})\text{NC}(=\text{O})\text{N}_1$.

Its calculated composition is

$$\begin{aligned} M(D) &= 4(12) + 4(1) + 2(14) + 3(16) = 128 \text{ g mol}^{-1}, \\ \%C &= 37.5, \quad \%H = 3.125, \quad \%N = 21.875, \end{aligned}$$

in agreement with the given percentages.

To draw the structure, make a six-membered ring with the successive atoms



Attach a carbonyl oxygen to C2, C4, and C6; one hydrogen to each nitrogen; and two hydrogens to C5. Mark either C5 hydrogen with an asterisk:



Loss of this proton gives the **barbiturate anion**, $\text{O}=\text{C}1[\text{CH}-]\text{C}(=\text{O})\text{NC}(=\text{O})\text{N}1$. Its negative charge is resonance-stabilized by the carbonyl groups on both sides of C5. This explains the characteristic acidity of the methylene hydrogen.

For completeness, the inorganic species used in the equations have the following names and SMILES:

Species	SMILES
Water, H_2O	<chem>O</chem>
Hydrogen ion, H^+	<chem>[H+]</chem>
Hydroxide ion, OH^-	<chem>[OH-]</chem>
Iodine, I_2	<chem>I I</chem>
Iodide ion, I^-	<chem>[I-]</chem>
Sodium atom, Na	<chem>[Na]</chem>
Sodium ion, Na^+	<chem>[Na+]</chem>
Hydrogen, H_2	<chem>[H][H]</chem>
Ammonia, NH_3	<chem>N</chem>
Ammonium ion, NH_4^+	<chem>[NH4+]</chem>
Carbonate ion, CO_3^{2-}	<chem>[O-]C(=O)[O-]</chem>
Carbon dioxide, CO_2	<chem>O=C=O</chem>

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

Problem 7: Solubility of calcium oxalate and protolysis of oxalate

Calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is a sparingly soluble salt of analytical and physiological importance. The solubility product is 2.1×10^{-9} at 25 °C. Oxalate ions can protolyse to form hydrogen oxalate ions and oxalic acid. The pK_a values at 25 °C are 1.23 ($\text{H}_2\text{C}_2\text{O}_4$) and 4.28 (HC_2O_4^-). At 25 °C the ionic product of water is 1.0×10^{-14} .

7.1 State those expressions for the equilibrium conditions which are of interest for the calculation of the solubility of calcium oxalate monohydrate.

7.2 State the concentration conditions which are necessary for the calculation of the solubility s (in mol dm^{-3}) of calcium oxalate in a strong acid of concentration C .

7.3 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in a plant cell in which the buffer system regulates the pH to 6.5.

7.4 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in hydrochloric acid with a concentration of $0.010 \text{ mol dm}^{-3}$. Give the concentration of hydrogen ions in the solution.

7.5 Calculate the equilibrium concentrations of all other species in solution d).

Official English text of the problem.

Answers

Define

$$h = [\text{H}^+], \quad x = [\text{C}_2\text{O}_4^{2-}], \quad y = [\text{HC}_2\text{O}_4^-], \quad z = [\text{H}_2\text{C}_2\text{O}_4].$$

Concentrations are expressed in mol dm^{-3} .

• 7.1

$$[\text{Ca}^{2+}]x = K_{\text{sp}} = 2.1 \times 10^{-9},$$
$$\frac{hy}{z} = K_{a1} = 10^{-1.23}, \quad \frac{hx}{y} = K_{a2} = 10^{-4.28}, \quad h[\text{OH}^-] = K_w = 1.0 \times 10^{-14}.$$

• 7.2 For a fully dissociated monoprotic strong acid:

$$[\text{Ca}^{2+}] = s = x + y + z,$$
$$h + 2s = C + [\text{OH}^-] + y + 2x.$$

Equivalently, the proton balance is

$$h + y + 2z = C + [\text{OH}^-].$$

• 7.3

$$6.7 \times 10^{-3} \text{ g dm}^{-3}$$

of calcium oxalate monohydrate.

• 7.4

$$9.6 \times 10^{-2} \text{ g dm}^{-3}, \quad [\text{H}^+] = 9.3 \times 10^{-3} \text{ mol dm}^{-3}.$$

• 7.5 The other equilibrium solute concentrations are:

Species	Concentration / mol dm^{-3}
Ca^{2+}	6.6×10^{-4}
$\text{C}_2\text{O}_4^{2-}$	3.2×10^{-6}
HC_2O_4^-	5.6×10^{-4}
$\text{H}_2\text{C}_2\text{O}_4$	8.9×10^{-5}
OH^-	1.1×10^{-12}
Cl^-	1.0×10^{-2}

Solution

We use the concentration-based equilibrium model implied by the supplied constants, taking the activities of the pure solid and water as unity. Dissolved calcium is treated as free calcium ions, and dissolved oxalate is distributed among its three protonation states.

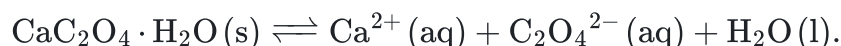
The species and their structural representations are:

Name	Formula	SMILES
Calcium oxalate monohydrate	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	<chem>[Ca+2].[O-]C(=O)C(=O)[O-].O</chem>
Calcium ion	Ca^{2+}	<chem>[Ca+2]</chem>
Oxalate ion	$\text{C}_2\text{O}_4^{2-}$	<chem>[O-]C(=O)C(=O)[O-]</chem>
Hydrogen oxalate ion	HC_2O_4^-	<chem>O=C(O)C(=O)[O-]</chem>
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	<chem>O=C(O)C(=O)O</chem>
Hydrogen ion (proton)	H^+	<chem>[H+]</chem>
Hydroxide ion	OH^-	<chem>[OH-]</chem>
Water	H_2O	<chem>O</chem>
Hydrogen chloride	HCl	<chem>Cl</chem>
Chloride ion	Cl^-	<chem>[Cl-]</chem>

The hydrate SMILES lists its components; it does not describe the crystal lattice or calcium coordination geometry. In aqueous equations, H^+ denotes hydrated protons, conventionally represented by hydronium, H_3O^+ , [OH3+].

7.1 — Equilibrium conditions

Dissolution of the monohydrate is



Consequently,

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.1 \times 10^{-9}.$$

The two acid-dissociation equilibria are

$$\begin{aligned} \text{H}_2\text{C}_2\text{O}_4(\text{aq}) &\rightleftharpoons \text{H}^+(\text{aq}) + \text{HC}_2\text{O}_4^-(\text{aq}), \\ K_{a1} &= \frac{[\text{H}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = 10^{-1.23} = 5.8884 \times 10^{-2}, \end{aligned}$$

and

$$\begin{aligned} \text{HC}_2\text{O}_4^-(\text{aq}) &\rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}), \\ K_{a2} &= \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = 10^{-4.28} = 5.2481 \times 10^{-5}. \end{aligned}$$

The reverse directions describe the successive protonation of oxalate.

Finally, water ionization gives



7.2 — Concentration conditions

Each mole of dissolved salt supplies one mole of calcium and one mole of total oxalate. Thus, in the absence of other calcium or oxalate sources,

$$\boxed{[\text{Ca}^{2+}] = s}, \quad \boxed{x + y + z = s}.$$

For a fully dissociated monoprotic strong acid of analytical concentration C , the spectator anion contributes a negative-charge concentration C . Electroneutrality therefore requires

$$h + 2s = C + [\text{OH}^-] + y + 2x.$$

Substituting $s = x + y + z$ gives the equivalent proton balance:

$$h + y + 2z = C + [\text{OH}^-].$$

Here, each hydrogen oxalate ion contains one proton taken up by oxalate, and each oxalic acid molecule contains two.

To obtain a useful solubility expression, use the acid equilibria:

$$y = \frac{h}{K_{a2}}x, \quad z = \frac{h^2}{K_{a1}K_{a2}}x.$$

Define

$$D(h) = 1 + \frac{h}{K_{a2}} + \frac{h^2}{K_{a1}K_{a2}}.$$

Then

$$s = xD(h).$$

Since $sx = K_{\text{sp}}$,

$$s = \sqrt{K_{\text{sp}}D(h)}, \quad x = \frac{K_{\text{sp}}}{s}.$$

Protonation lowers the fraction of dissolved oxalate present as $\text{C}_2\text{O}_4^{2-}$, allowing more solid to dissolve while maintaining the solubility product.

7.3 — Solubility at buffered pH 6.5

The buffer fixes

$$h = 10^{-6.5} = 3.1623 \times 10^{-7} \text{ mol dm}^{-3}.$$

Therefore,

$$D(h) = 1 + \frac{3.1623 \times 10^{-7}}{5.2481 \times 10^{-5}} + \frac{(3.1623 \times 10^{-7})^2}{(5.8884 \times 10^{-2})(5.2481 \times 10^{-5})} = 1.0060256.$$

The molar solubility is

$$s = \sqrt{(2.1 \times 10^{-9})(1.0060256)} = 4.5964 \times 10^{-5} \text{ mol dm}^{-3}.$$

Using the molar mass of the **monohydrate**,

$$M(\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}) = 146.11 \text{ g mol}^{-1},$$

the mass solubility is

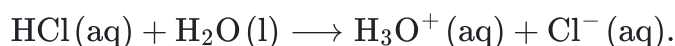
$$sM = (4.5964 \times 10^{-5})(146.11) = 6.7157 \times 10^{-3} \text{ g dm}^{-3}.$$

Thus,

$$\text{Solubility} = 6.7 \times 10^{-3} \text{ g dm}^{-3}.$$

7.4 — Solubility in $0.010 \text{ mol dm}^{-3}$ hydrochloric acid

Hydrogen chloride dissociates completely:



Hence,

$$[\text{Cl}^-] = C = 0.010 \text{ mol dm}^{-3}.$$

The free hydrogen-ion concentration must be calculated because oxalate takes up some of the added protons. Substituting the equilibrium expressions into the proton balance gives

$$h + \frac{K_{\text{sp}}}{s} \left(\frac{h}{K_{a2}} + \frac{2h^2}{K_{a1}K_{a2}} \right) = C + \frac{K_w}{h},$$

where

$$s = \sqrt{K_{\text{sp}} \left(1 + \frac{h}{K_{a2}} + \frac{h^2}{K_{a1}K_{a2}} \right)}.$$

Solving this single equation for h , retaining guard digits, gives

$$h = 9.258101 \times 10^{-3} \text{ mol dm}^{-3},$$
$$D(h) = 205.1455,$$

and therefore

$$s = \sqrt{(2.1 \times 10^{-9})(205.1455)} = 6.563578 \times 10^{-4} \text{ mol dm}^{-3}.$$

The mass solubility is

$$sM = (6.563578 \times 10^{-4})(146.11) = 0.0959004 \text{ g dm}^{-3}.$$

To appropriate significant figures,

$$\boxed{\text{Solubility} = 0.096 \text{ g dm}^{-3}}, \quad \boxed{[\text{H}^+] = 0.0093 \text{ mol dm}^{-3}}.$$

7.5 — Other equilibrium concentrations in the hydrochloric acid solution

Using the unrounded values from 7.4,

$$[\text{Ca}^{2+}] = s = 6.563578 \times 10^{-4} \text{ mol dm}^{-3},$$
$$[\text{C}_2\text{O}_4^{2-}] = \frac{K_{\text{sp}}}{s} = 3.199475 \times 10^{-6} \text{ mol dm}^{-3},$$
$$[\text{HC}_2\text{O}_4^-] = \frac{h[\text{C}_2\text{O}_4^{2-}]}{K_{a2}} = 5.644177 \times 10^{-4} \text{ mol dm}^{-3},$$
$$[\text{H}_2\text{C}_2\text{O}_4] = \frac{h[\text{HC}_2\text{O}_4^-]}{K_{a1}} = 8.874063 \times 10^{-5} \text{ mol dm}^{-3},$$
$$[\text{OH}^-] = \frac{K_w}{h} = 1.080135 \times 10^{-12} \text{ mol dm}^{-3},$$

and

$$[\text{Cl}^-] = 0.010 \text{ mol dm}^{-3}.$$

These give the rounded concentrations listed in **Answers**. As checks, the oxalate balance is

$$x + y + z = 6.563578 \times 10^{-4} \text{ mol dm}^{-3} = s,$$

and the proton balance is

$$h + y + 2z - [\text{OH}^-] = 0.0100000 \text{ mol dm}^{-3} = C.$$

Water is the solvent, with unit activity in this model; no separate undissociated hydrogen chloride concentration is retained under the complete-dissociation assumption.

The solution was checked against the official solution.