

IChO 1978

Theory problems and solutions · Toruń, Poland · 5 theory problems with complete solutions

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Problem 1: Analysis of a chromium ore

- a) A chromium ore which does not contain water, consists of: $\text{Fe}(\text{CrO}_2)_2$, $\text{Mg}(\text{CrO}_2)_2$, MgCO_3 , and CaSiO_3 .
- b) It was found by analysis the ore contains 45.6 % of Cr_2O_3 , 7.98 % of Fe_2O_3 , and 16.12 % of MgO .
- c) When the ore was treated with a concentrated hydrochloric acid, chromium compounds being present in the ore did not react with the acid.
- d) When the reaction was finished, the ore was thoroughly washed with water (till the reaction with Cl^- was negative) and the solid residue was dried to a constant mass.

Problems:

1.1 Write stoichiometric and ionic equations for the reactions taking place when the ore is treated with the hydrochloric acid as given in c).

1.2 Calculate:

- the content of the compounds (in mass %) present in the ore,
- amounts of substances of the compounds present in the ore.

1.3 Calculate the content of Cr_2O_3 (in mass %) in the dried residue obtained according to d).

1.4 A glass tube was filled with a sufficient amount of granulated CaO , the total mass of the filled tube having been 412.02 g. A gas formed by the reaction as given in c), was dried and then transmitted through the glass tube. Calculate the mass of the glass tube with its filling after the reaction was finished.

Relative atomic masses:

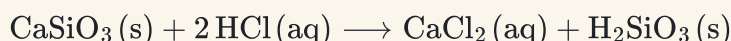
$$A_r(\text{Cr}) = 52.01; \quad A_r(\text{Fe}) = 55.85; \quad A_r(\text{Mg}) = 24.32; \quad A_r(\text{Ca}) = 40.08;$$

$$A_r(\text{Si}) = 28.09; \quad A_r(\text{C}) = 12.01; \quad A_r(\text{O}) = 16.00.$$

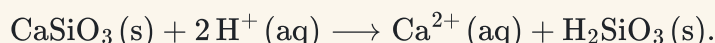
Official English text of the problem.

Answers

- 1.1 The molecular equations are



and the net ionic equations are



Here H_2SiO_3 conventionally represents precipitated hydrated silica. Both chromites remain unchanged.

- 1.2 On a **100 g ore basis**:

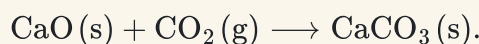
Compound	Mass percentage	Amount per 100 g ore
Iron(II) chromite, $\text{Fe}(\text{CrO}_2)_2$	22.4%	0.0999 mol
Magnesium chromite, $\text{Mg}(\text{CrO}_2)_2$	38.5%	0.200 mol
Magnesium carbonate, MgCO_3	16.8%	0.200 mol
Calcium silicate, CaSiO_3	22.3%	0.192 mol

For an ore sample of mass m , multiply these amounts by $m/(100 \text{ g})$.

- 1.3 Assuming the hydrated silica is dried to anhydrous silicon dioxide, SiO_2 ,

$$w(\text{Cr}_2\text{O}_3) = 63.0\%.$$

- 1.4 Calcium oxide absorbs the carbon dioxide:



For an ore sample of mass m ,

$$m_{\text{tube,final}} = 412.02 \text{ g} + 0.08792 m.$$

If $m = 100 \text{ g}$, the final mass is 420.81 g. The supplied statement does not specify the ore mass, so an unconditional numerical answer is unavailable.

Solution

1.1 — Reactions with hydrochloric acid

The two chromites do not react, as explicitly stated in the problem.

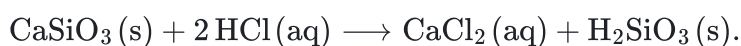
Magnesium carbonate reacts with acid because protonation of carbonate produces carbon dioxide and water. Magnesium chloride remains in solution:



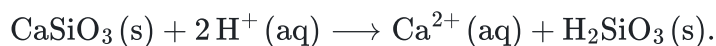
Removing the spectator chloride ions gives



Calcium silicate reacts with acid to give soluble calcium chloride and insoluble hydrated silica, conventionally written as metasilicic acid:



Its net ionic equation is



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

Species	Name	SMILES
HCl	Hydrogen chloride; its aqueous solution is hydrochloric acid	Cl
H ⁺	Hydrogen ion	[H+]
Cl ⁻	Chloride ion	[Cl-]
Mg ²⁺	Magnesium(II) ion	[Mg+2]
Ca ²⁺	Calcium(II) ion	[Ca+2]
CO ₃ ²⁻	Carbonate ion, present in the carbonate salts	[O-]C(=O)[O-]
CO ₂	Carbon dioxide	O=C=O
H ₂ O	Water	O

Formal monomeric **metasilicic acid**, H₂SiO₃, can be represented by O[Si](=O)O. The actual precipitate is a hydrated silica network; this molecular SMILES does not describe its polymeric structure. Likewise, the crystalline salts, chromites, and solid oxides are extended solids whose crystal structures cannot be specified by a single molecular SMILES. Aqueous hydration is also not shown by the ionic SMILES.

1.2 — Composition and amounts of substances

Choose **100 g of ore** as the calculation basis. This is a convenient normalization, since no actual sample mass is given.

The reported oxide percentages are **analytical equivalents**, not additional compounds in the ore. Thus the analysis corresponds to:

$$m(\text{Cr}_2\text{O}_3) = 45.6 \text{ g}, \quad m(\text{Fe}_2\text{O}_3) = 7.98 \text{ g}, \quad m(\text{MgO}) = 16.12 \text{ g}.$$

Use the shorter formulas FeCr₂O₄ and MgCr₂O₄ for the two chromites. Let their amounts be x and y , and let the amounts of magnesium carbonate and calcium silicate be z and t , respectively.

The required molar masses, calculated from the supplied atomic masses, are:

Compound	Molar mass / g mol ⁻¹
Cr ₂ O ₃	152.02
Fe ₂ O ₃	159.70
MgO	40.32
FeCr ₂ O ₄	223.87
MgCr ₂ O ₄	192.34
MgCO ₃	84.33
CaSiO ₃	116.17

All iron occurs in iron(II) chromite. One mole of iron(III) oxide equivalent represents two moles of iron, so

$$x = 2 \frac{7.98 \text{ g}}{159.70 \text{ g mol}^{-1}} = 0.0999374 \text{ mol}.$$

Each mole of either chromite contains two chromium atoms and therefore corresponds to one mole of chromium(III) oxide equivalent:

$$x + y = \frac{45.6 \text{ g}}{152.02 \text{ g mol}^{-1}} = 0.2999605 \text{ mol.}$$

Hence

$$y = 0.2999605 - 0.0999374 = 0.2000231 \text{ mol.}$$

Magnesium occurs in magnesium chromite and magnesium carbonate. Each contains one magnesium atom per formula unit, giving

$$y + z = \frac{16.12 \text{ g}}{40.32 \text{ g mol}^{-1}} = 0.3998016 \text{ mol,}$$

and therefore

$$z = 0.3998016 - 0.2000231 = 0.1997784 \text{ mol.}$$

Keeping guard digits, the masses are

$$\begin{aligned} m(\text{FeCr}_2\text{O}_4) &= (0.0999374)(223.87) \text{ g} = 22.37298 \text{ g,} \\ m(\text{MgCr}_2\text{O}_4) &= (0.2000231)(192.34) \text{ g} = 38.47245 \text{ g,} \\ m(\text{MgCO}_3) &= (0.1997784)(84.33) \text{ g} = 16.84732 \text{ g.} \end{aligned}$$

Since these and calcium silicate are the only constituents,

$$m(\text{CaSiO}_3) = 100 - 22.37298 - 38.47245 - 16.84732 = 22.30725 \text{ g,}$$

so

$$t = \frac{22.30725 \text{ g}}{116.17 \text{ g mol}^{-1}} = 0.1920225 \text{ mol.}$$

On the 100 g basis, the numerical masses in grams equal the mass percentages. Rounding gives the results listed in **Answers**.

1.3 — Chromium content of the dried residue

Washing removes dissolved magnesium chloride, calcium chloride, and excess hydrochloric acid. The residue contains the two unchanged chromites and the silica precipitate.

Using the conventional assumption that drying dehydrates the silica,



Each mole of calcium silicate therefore leaves one mole of silicon dioxide. Its molar mass is

$$M(\text{SiO}_2) = 28.09 + 2(16.00) = 60.09 \text{ g mol}^{-1},$$

and its mass is

$$m(\text{SiO}_2) = (0.1920225 \text{ mol})(60.09 \text{ g mol}^{-1}) = 11.53863 \text{ g.}$$

Thus

$$m_{\text{residue}} = 22.37298 + 38.47245 + 11.53863 = 72.38406 \text{ g.}$$

All chromium remains in the residue, so its chromium(III) oxide equivalent is still 45.6 g:

$$w(\text{Cr}_2\text{O}_3) = \frac{45.6}{72.38406} \times 100\% = 62.9973\% \approx \boxed{63.0\%}.$$

This percentage expresses the chromium content **as oxide equivalent**; it does not imply that free chromium(III) oxide was produced.

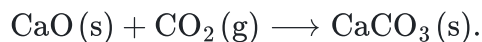
1.4 — Final mass of the absorption tube

The evolved gas is carbon dioxide, produced solely by magnesium carbonate:

$$n(\text{CO}_2) = n(\text{MgCO}_3) = 0.1997784 \text{ mol}$$

per 100 g of ore.

The gas is dried, then absorbed by calcium oxide to form calcium carbonate:



Because sufficient calcium oxide is present, the tube gains the entire mass of the carbon dioxide. Using

$$M(\text{CO}_2) = 12.01 + 2(16.00) = 44.01 \text{ g mol}^{-1},$$

the gain per 100 g of ore is

$$\Delta m = (0.1997784 \text{ mol})(44.01 \text{ g mol}^{-1}) = 8.79225 \text{ g}.$$

Consequently, for an actual ore mass m ,

$$m_{\text{tube,final}} = 412.02 \text{ g} + (8.79225 \text{ g}) \frac{m}{100 \text{ g}}.$$

For a **100 g sample**, this becomes

$$m_{\text{tube,final}} = 412.02 + 8.79225 \approx \boxed{420.81 \text{ g}}.$$

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

Problem 2: Water hardness caused by Fe^{2+} and Ca^{2+}

A sample of water under investigation had 10° of temporary hardness and 10° of permanent hardness. Hardness of the water was caused by cations Fe^{2+} and Ca^{2+} only.

A volume of 10.00 dm³ of the water was at disposal. From this volume 100.00 cm³ were taken for further procedure. The water was oxidised with a H_2O_2 solution and then precipitated with an aqueous ammonia solution. A brown precipitate was dried and after an appropriate heating 0.01432 g of an anhydrous product was obtained.

Problems:

2.1 Calculate the molar ratio of Fe^{2+} : Ca^{2+} in the water under investigation.

2.2 In another experiment, 10.00 dm³ of the water was used again. The temporary hardness caused by cations Ca^{2+} was removed first and the permanent hardness caused by cations Fe^{2+} was removed by addition of Na_3PO_4 . Calculate the mass of the precipitate (in its anhydrous form) on the assumption that only one half of cations Fe^{2+} was oxidised to Fe^{3+} in 10.00 dm³ of the water analysed.

Calculation should be made with an accuracy of one hundredth. Give the molar ratio in integers.

1° of hardness = 10 mg CaO in 1 dm³ of water.

Relative atomic masses:

$$\begin{array}{lll} A_r(\text{Ca}) = 40.08; & A_r(\text{Fe}) = 55.85; & A_r(\text{C}) = 12.01; \\ A_r(\text{H}) = 1.01; & A_r(\text{P}) = 31.00; & A_r(\text{O}) = 16.00. \end{array}$$

Official English text of the problem.

Answers

- **2.1:** The intended integer molar ratio is approximately

$$\text{Fe}^{2+} : \text{Ca}^{2+} = 1 : 1.$$

The printed numerical data give 1.01150 : 1.

- **2.2:** The combined anhydrous precipitates from both removal stages weigh

$$4.20 \text{ g}.$$

The iron phosphate precipitate alone weighs 2.42 g . These results retain the measured iron content and total hardness.

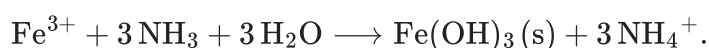
Solution

2.1 — Determination of the iron-to-calcium ratio

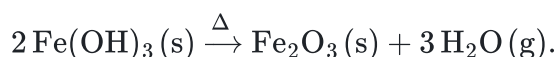
Hydrogen peroxide oxidises iron(II) to iron(III). The balanced oxidation equation, written in acidic form, is



Aqueous ammonia then precipitates brown hydrous iron(III) hydroxide, conventionally represented as $\text{Fe}(\text{OH})_3$:



In the intended gravimetric procedure, calcium remains in solution. Heating the iron precipitate removes water and gives anhydrous iron(III) oxide:



Thus the weighed product is Fe_2O_3 , with molar mass

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

The amount of iron originally present in the 100.00 cm^3 aliquot is therefore

$$n_{\text{Fe}} = 2n(\text{Fe}_2\text{O}_3) = \frac{2(0.01432 \text{ g})}{159.70 \text{ g mol}^{-1}} = 1.7933626 \times 10^{-4} \text{ mol}.$$

The total hardness is

$$10^\circ + 10^\circ = 20^\circ,$$

equivalent to 200 mg of CaO per cubic decimetre. The aliquot consequently contains

$$m_{\text{CaO, equiv}} = (0.200 \text{ g dm}^{-3})(0.10000 \text{ dm}^3) = 0.02000 \text{ g}.$$

Both hardness-producing cations are divalent, so one mole of either contributes the same hardness as one mole of CaO . Since

$$M(\text{CaO}) = 40.08 + 16.00 = 56.08 \text{ g mol}^{-1},$$

we obtain

$$n_{\text{Fe}} + n_{\text{Ca}} = \frac{0.02000}{56.08} = 3.5663338 \times 10^{-4} \text{ mol}.$$

Hence

$$n_{\text{Ca}} = (3.5663338 - 1.7933626) \times 10^{-4} = 1.7729713 \times 10^{-4} \text{ mol},$$

and

$$\frac{n_{\text{Fe}}}{n_{\text{Ca}}} = \frac{1.7933626}{1.7729713} = 1.01150.$$

The intended simple integer ratio is therefore approximately

$$\boxed{\text{Fe}^{2+} : \text{Ca}^{2+} = 1 : 1}.$$

The unrounded amounts, rather than an imposed exact 1 : 1 ratio, are used below.

2.2 — Mass of the anhydrous precipitates

The volume in this experiment is 100 times the aliquot volume. Therefore,

$$n_{\text{Fe, total}} = 0.017933626 \text{ mol}, \quad n_{\text{Ca}} = 0.017729713 \text{ mol}.$$

Temporary calcium hardness is removed by heating, which precipitates calcium carbonate:



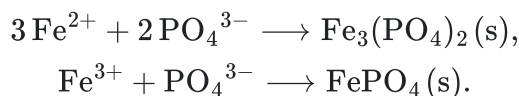
Its molar mass and precipitated mass are

$$\begin{aligned} M(\text{CaCO}_3) &= 40.08 + 12.01 + 3(16.00) = 100.09 \text{ g mol}^{-1}, \\ m(\text{CaCO}_3) &= (0.017729713)(100.09) = 1.774567 \text{ g}. \end{aligned}$$

Half the iron remains iron(II), and half is oxidised to iron(III):

$$n(\text{Fe}^{2+}) = n(\text{Fe}^{3+}) = \frac{0.017933626}{2} = 0.008966813 \text{ mol}.$$

Addition of trisodium phosphate supplies phosphate ions. The two precipitation reactions are



The products are iron(II) phosphate and iron(III) phosphate, respectively. Their amounts are

$$\begin{aligned} n(\text{Fe}_3(\text{PO}_4)_2) &= \frac{0.008966813}{3} = 0.002988938 \text{ mol}, \\ n(\text{FePO}_4) &= 0.008966813 \text{ mol}. \end{aligned}$$

Using anhydrous formula masses,

$$\begin{aligned} M(\text{Fe}_3(\text{PO}_4)_2) &= 3(55.85) + 2[31.00 + 4(16.00)] = 357.55 \text{ g mol}^{-1}, \\ M(\text{FePO}_4) &= 55.85 + 31.00 + 4(16.00) = 150.85 \text{ g mol}^{-1}. \end{aligned}$$

Thus,

$$\begin{aligned} m(\text{Fe}_3(\text{PO}_4)_2) &= (0.002988938)(357.55) = 1.068695 \text{ g}, \\ m(\text{FePO}_4) &= (0.008966813)(150.85) = 1.352644 \text{ g}. \end{aligned}$$

The phosphate precipitate alone therefore weighs

$$\boxed{m_{\text{phosphates}} = 1.068695 + 1.352644 = 2.421338 \text{ g} \approx 2.42 \text{ g}}.$$

Including the calcium carbonate precipitated during the first stage gives

$$\boxed{m_{\text{all precipitates}} = 1.774567 + 2.421338 = 4.195905 \text{ g} \approx 4.20 \text{ g}}.$$

Names and SMILES of the chemical species used

For ionic solids, the disconnected SMILES below represent formal formula units. They do not describe the crystal lattice, hydration, or metal coordination geometry; hydrous iron(III) hydroxide is not a discrete molecular species.

Species and name	SMILES
Fe^{2+} , iron(II) ion	[Fe+2]
Fe^{3+} , iron(III) ion	[Fe+3]
Ca^{2+} , calcium ion	[Ca+2]
H^+ , hydrogen ion	[H+]
H_2O_2 , hydrogen peroxide	OO
H_2O , water	O
NH_3 , ammonia	N
NH_4^+ , ammonium ion	[NH4+]
$\text{Fe}(\text{OH})_3$, iron(III) hydroxide	[Fe+3].[OH-].[OH-].[OH-]
Fe_2O_3 , iron(III) oxide	[Fe+3].[Fe+3].[O-2].[O-2].[O-2]
CaO , calcium oxide	[Ca+2].[O-2]
HCO_3^- , hydrogen carbonate ion	OC(=O)[O-]
CO_2 , carbon dioxide	O=C=O
CaCO_3 , calcium carbonate	[Ca+2].[O-]C(=O)[O-]
Na_3PO_4 , trisodium phosphate	[Na+].[Na+].[Na+].[O-]P(=O)([O-])[O-]
PO_4^{3-} , phosphate ion	[O-]P(=O)([O-])[O-]
$\text{Fe}_3(\text{PO}_4)_2$, iron(II) phosphate	[Fe+2].[Fe+2].[Fe+2].[O-]P(=O)([O-])[O-].[O-]P(=O)([O-])[O-]
FePO_4 , iron(III) phosphate	[Fe+3].[O-]P(=O)([O-])[O-]

The solution was checked against the official solution.

Problem 3: Chromium plating

Chromium plating is usually made by electrolysis in a solution of chromic acid. The chromium plated objects form the cathode. The anode is an alloy that is inert under given conditions, i. e. it does not react either chemically or electrochemically.

An electrolytic cell was filled with 100.0 dm^3 of an aqueous solution which contained 0.230 kg of chromium acid anhydride in 1 dm^3 of the solution.

In electrolysis a current of 1500 A passed through the electrolyte for 10.0 hours . After electrolysis an increase of the mass of the cathode was 0.679 kg .

The ratio of gas volumes

$$\frac{V_C}{V_A} = 1.603$$

where V_C is a volume of gases evolved at the cathode, whereas that marked as V_A is the volume of gases which are evolved at the anode. Both volumes were measured at the same conditions.

Problems

3.1 What part of the total charge (in %) was used for a deposition of 0.679 kg of chromium?

3.2 Calculate:

a) the volume ratio of both gases (at STP) which are evolved as by-products at the cathode and anode,

b) current efficiency for the corresponding reactions taking place separately at the cathode and anode when the gases are evolved.

If you find any disproportion between the data calculated and those given in the task, try to explain what process would take place in the electrolytic cell which has not been considered till now.

Write the corresponding summary equation for the reactions at electrodes and correct your previous calculations if possible.

Official English text of the problem.

Answers

- **3.1:** The fraction of charge used to deposit chromium is 14.0%.
- **3.2(a):** The gases are hydrogen at the cathode and oxygen at the anode. Considering only chromium deposition and gas evolution predicts $V_C/V_A = 1.720$. Including the closed chromium(VI)/chromium(III) cycle gives the measured ratio 1.603, with corrected STP volumes

$$V_C = 3.55 \times 10^3 \text{ dm}^3, \quad V_A = 2.21 \times 10^3 \text{ dm}^3.$$

- **3.2(b):** The initial gas current efficiencies are 86.0% for hydrogen and 100% for oxygen. The corrected efficiencies are

$$\eta_{\text{H}_2} = 56.5\%, \quad \eta_{\text{O}_2} = 70.5\%.$$

Chromium(VI) reduction to chromium(III) and its reverse oxidation consume 29.5% of the charge at each respective electrode.

Solution

Use

$$F = 96485 \text{ C mol}^{-1}, \quad M(\text{Cr}) = 52.00 \text{ g mol}^{-1},$$

and the ideal-gas molar volume $V_m = 22.414 \text{ dm}^3 \text{ mol}^{-1}$ at STP, taken here as 273.15 K and 1 atm.

The chemical species used below are:

Species	Name	SMILES
CrO_3	Chromium(VI) oxide, chromic acid anhydride	<chem>O=[Cr](=O)=O</chem>
H_2CrO_4	Chromic acid	<chem>O=[Cr](=O)(O)O</chem>
Cr^{3+}	Chromium(III) ion	<chem>[Cr+3]</chem>
H^+	Hydrogen ion, proton	<chem>[H+]</chem>
H_2O	Water	<chem>O</chem>
H_2	Hydrogen	<chem>[H][H]</chem>
O_2	Oxygen	<chem>O=O</chem>
Cr	Chromium	<chem>[Cr]</chem>

The ion SMILES omit hydration, and [Cr] represents an atom rather than a metallic lattice. The oxide SMILES is a formal molecular representation; O=O does not specify oxygen's triplet ground state. Dissolved chromium(VI) is represented formally as H_2CrO_4 in the balances below.

3.1 — Charge used for chromium deposition

Chromium starts in oxidation state +6, so its net reduction to the metal requires six electrons per chromium atom:



The total charge passed is

$$Q = It = (1500\text{ A})(10.0 \times 3600\text{ s}) = 5.40 \times 10^7\text{ C}.$$

The amount of deposited chromium is

$$n_{\text{Cr}} = \frac{679\text{ g}}{52.00\text{ g mol}^{-1}} = 13.0577\text{ mol}.$$

Consequently,

$$Q_{\text{Cr}} = 6Fn_{\text{Cr}} = 7.559 \times 10^6\text{ C},$$

and

$$\eta_{\text{Cr}} = \frac{Q_{\text{Cr}}}{Q} \times 100\% = 14.0\%.$$

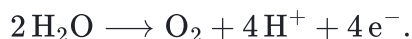
This is the charge requirement for the overall reduction from chromium(VI) to chromium metal, regardless of intermediate reduction steps.

3.2(a) — Initial calculation of the gas-volume ratio

In the acidic electrolyte, hydrogen is evolved at the cathode:



At the inert anode, water can be oxidized to oxygen:



Initially suppose that these gas-producing reactions and chromium deposition are the only electrode reactions. Then

$$\begin{aligned} n_{\text{H}_2}^{(0)} &= \frac{Q - Q_{\text{Cr}}}{2F} = 240.66\text{ mol}, \\ n_{\text{O}_2}^{(0)} &= \frac{Q}{4F} = 139.92\text{ mol}. \end{aligned}$$

At the same temperature and pressure, gas volumes are proportional to amounts. Therefore,

$$\begin{aligned} \left(\frac{V_{\text{C}}}{V_{\text{A}}} \right)_0 &= \frac{(Q - Q_{\text{Cr}})/(2F)}{Q/(4F)} \\ &= 2 \left(1 - \frac{Q_{\text{Cr}}}{Q} \right) \\ &= \boxed{1.720}. \end{aligned}$$

The corresponding initial STP volumes would be approximately $5.39 \times 10^3\text{ dm}^3$ of hydrogen and $3.14 \times 10^3\text{ dm}^3$ of oxygen. Their ratio differs from the measured 1.603.

3.2(b) — Initial current efficiencies

Under the same initial assumptions,

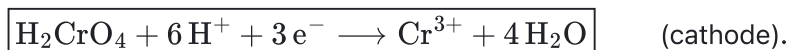
$$\eta_{\text{H}_2}^{(0)} = \frac{Q - Q_{\text{Cr}}}{Q} \times 100\% = \boxed{86.0\%},$$

$$\eta_{\text{O}_2}^{(0)} = \frac{Q}{Q} \times 100\% = \boxed{100\%}.$$

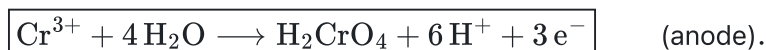
The discrepancy shows that this reaction model is incomplete.

3.2 — Additional electrode reactions and corrected calculation

Chromium(VI) can also be reduced to dissolved chromium(III), without depositing metal or evolving gas:



The chromium(III) can then be reoxidized at the anode:



An inert anode can support this oxidation of a dissolved species while remaining chemically unchanged itself.

For a **closed redox cycle**, with no net accumulation of chromium(III), equal amounts of chromium undergo these opposite three-electron reactions. Thus the same charge Q_s is assigned to the cycle at each electrode.

Define the charge fractions

$$d = \frac{Q_{\text{Cr}}}{Q} = 0.139986, \quad s = \frac{Q_s}{Q}.$$

The separate electrode charge balances give

$$\eta_{\text{H}_2} = 1 - d - s, \quad \eta_{\text{O}_2} = 1 - s,$$

where efficiencies here are fractions rather than percentages. Since hydrogen requires two electrons per molecule and oxygen evolution supplies four,

$$1.603 = \frac{V_{\text{C}}}{V_{\text{A}}} = 2 \frac{1 - d - s}{1 - s}.$$

Rearranging,

$$(2 - 1.603)(1 - s) = 2d,$$

so

$$1 - s = \frac{2(0.139986)}{0.397} = 0.705218, \quad s = 0.294782.$$

Therefore,

$$\boxed{\eta_{\text{O}_2} = 70.5\%},$$

$$\boxed{\eta_{\text{H}_2} = (1 - 0.139986 - 0.294782) \times 100\% = 56.5\%}.$$

The complete charge allocation is:

Electrode	Net process	Percentage of charge
Cathode	Chromium(VI) to deposited chromium	14.0%
Cathode	Chromium(VI) to chromium(III) in the cycle	29.5%
Cathode	Hydrogen evolution	56.5%
Anode	Chromium(III) to chromium(VI) in the cycle	29.5%
Anode	Oxygen evolution	70.5%

Each electrode's percentages sum to 100%.

The corrected amounts of gas are

$$n_{\text{H}_2} = \frac{\eta_{\text{H}_2} Q}{2F} = 158.172 \text{ mol},$$

$$n_{\text{O}_2} = \frac{\eta_{\text{O}_2} Q}{4F} = 98.6727 \text{ mol}.$$

Using unrounded values,

$$V_{\text{C}} = n_{\text{H}_2} V_{\text{m}} = 3545.28 \text{ dm}^3 \approx \boxed{3.55 \times 10^3 \text{ dm}^3},$$

$$V_{\text{A}} = n_{\text{O}_2} V_{\text{m}} = 2211.65 \text{ dm}^3 \approx \boxed{2.21 \times 10^3 \text{ dm}^3},$$

and

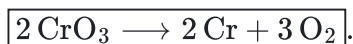
$$\frac{V_{\text{C}}}{V_{\text{A}}} = 1.603.$$

Overall reaction balance

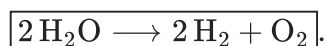
The two redox-cycle half-reactions cancel when added. Chromium deposition coupled to oxygen evolution gives



or, expressed using the original acid anhydride,



The accompanying net water electrolysis is



Thus a useful independent stoichiometric check is

$$n_{\text{O}_2} = \frac{3}{2} n_{\text{Cr}} + \frac{1}{2} n_{\text{H}_2},$$

which the corrected amounts satisfy.

The bath initially contains 23.0 kg of CrO_3 . Deposition consumes only

$$(13.0577 \text{ mol})(100.00 \text{ g mol}^{-1}) = 1.31 \text{ kg}$$

net; the closed chromium(VI)/chromium(III) cycle causes no additional net consumption.

The solution was checked against the official solution.

Problem 4: Thermal decomposition of ethane in a closed vessel

A vessel of a volume of 5.0 dm^3 was filled with ethane at a temperature of 300 K and normal pressure and sealed. The vessel with the gas was then heated and the pressure in it was measured at distinct temperatures. The following data were found:

T (K)	Pressure p , measured (kPa)	Pressure p' , calculated (kPa)
300	101.25	
500	169.20	
800	276.11	
1000	500.48	

Problems:

4.1 Calculate the pressure p' of ethane in the vessel according to the ideal gas law equation and fill in the values in a free column in the above table.

$$(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

4.2 Explain the differences between theoretical value p' and those (p) obtained by measurements.

4.3 Write the chemical equation for the reaction which takes place probably in the vessel at higher temperatures.

4.4 Calculate the value for the conversion degree α of ethane and that for equilibrium constant K_p of the reaction that takes place at temperatures of 800 and 1000 K.

4.5 The ratio of equilibrium constant K_p at two different temperatures is according to van't Hoff's equation equal to:

$$\ln \frac{K_1}{K_2} = \frac{\overline{\Delta H}}{R} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$(\ln = 2.303 \log)$$

Calculate the mean value $\overline{\Delta H}$ for reaction heat in the temperature range of 800 – 1000 K.

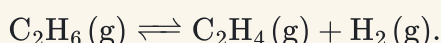
4.6 What influence will have an elevation of temperature and pressure on the conversion degree of ethane?

4.7 Calculate the relative error of the calculation.

Official English text of the problem.

Answers

- 4.1** At 300, 500, 800 and 1000 K, respectively: $p' = 101.25, 168.75, 270.00, 337.50 \text{ kPa}$.
- 4.2** Thermal decomposition increases the amount of gas, raising the pressure above the prediction for unchanged ethane.
- 4.3** Ethane C_2H_6 undergoes dehydrogenation to ethene $\text{C}=\text{C}$ and hydrogen $[\text{H}][\text{H}]$:



- 4.4** At 800 K: $\alpha = 0.0226 = 2.26\%$, $K_p = 0.141 \text{ kPa}$. At 1000 K: $\alpha = 0.483 = 48.3\%$, $K_p = 152 \text{ kPa}$. These K_p values use the pressure-quotient convention; dimensionless values for $p^\circ = 100 \text{ kPa}$ are 1.41×10^{-3} and 1.52.
- 4.5** $\overline{\Delta H} = +232 \text{ kJ mol}^{-1}$, per mole of ethane converted.
- 4.6** Increasing temperature increases conversion; increasing pressure by isothermal compression decreases conversion.
- 4.7** Interpreting "relative error" as $|p' - p|/p$, the values at 300, 500, 800 and 1000 K are 0, 0.266%, 2.21%, 32.6%, respectively. The requested error is not otherwise specified.

Solution

4.1

Let n_0 be the initial amount of ethane. For the reference calculation, its amount and the vessel volume remain constant:

$$p_0 V = n_0 R T_0, \quad p' V = n_0 R T.$$

Dividing eliminates both n_0 and V :

$$p' = p_0 \frac{T}{T_0} = (101.25 \text{ kPa}) \frac{T}{300 \text{ K}}.$$

The completed table is therefore:

T (K)	Measured p (kPa)	Calculated p' (kPa)
300	101.25	101.25
500	169.20	168.75
800	276.11	270.00
1000	500.48	337.50

4.2

The calculation above assumes that heating leaves the chemical composition unchanged. A reaction that produces more gas molecules increases the total amount of gas, and hence its pressure at a given temperature and volume:

$$p = \frac{n_{\text{total}}RT}{V}.$$

The excess pressures are

$$p - p' = 0, 0.45, 6.11, 162.98 \text{ kPa}$$

at the four successive temperatures. The substantial increase at high temperature is consistent with thermal decomposition of ethane.

The small discrepancy at 500 K could also include gas nonideality or experimental error. The supplied data do not separate these contributions. For the requested equilibrium calculations, we assume ideal-gas behavior and attribute the high-temperature excess pressure to the reaction below.

4.3

A probable reaction is dehydrogenation: ethane, C_2H_6 , loses hydrogen, $[\text{H}][\text{H}]$, to form the corresponding alkene, ethene, $\text{C}=\text{C}$:



The equation conserves both carbon and hydrogen. Each mole of ethane converted produces two moles of gaseous products, giving a net increase of one mole of gas. This explains the observed pressure increase.

4.4

Define the conversion degree by

$$\alpha = \frac{\text{amount of ethane converted}}{n_0}.$$

Starting from pure ethane, the amounts are:

State	C_2H_6	C_2H_4	H_2
Initially	n_0	0	0
At equilibrium	$n_0(1 - \alpha)$	$n_0\alpha$	$n_0\alpha$

Thus,

$$n_{\text{total}} = n_0(1 + \alpha), \quad p = p'(1 + \alpha),$$

and

$$\alpha = \frac{p - p'}{p'}.$$

At 800 K,

$$\alpha_{800} = \frac{276.11 - 270.00}{270.00} = 0.0226296 \approx \boxed{2.26\%}.$$

At 1000 K,

$$\alpha_{1000} = \frac{500.48 - 337.50}{337.50} = 0.482904 \approx \boxed{48.3\%}.$$

For ideal gases, each partial pressure is its amount multiplied by RT/V . Therefore,

$$p_{\text{C}_2\text{H}_6} = (1 - \alpha)p' = 2p' - p,$$

$$p_{\text{C}_2\text{H}_4} = p_{\text{H}_2} = \alpha p' = p - p'.$$

Using the pressure-quotient convention,

$$K_p = \frac{p_{\text{C}_2\text{H}_4} p_{\text{H}_2}}{p_{\text{C}_2\text{H}_6}} = \frac{\alpha^2 p'}{1 - \alpha} = \frac{\alpha^2 p}{1 - \alpha^2} = \boxed{\frac{(p - p')^2}{2p' - p}}.$$

The partial pressures are:

T (K)	$p_{\text{C}_2\text{H}_6}$ (kPa)	$p_{\text{C}_2\text{H}_4}$ (kPa)	p_{H_2} (kPa)
800	263.89	6.11	6.11
1000	174.52	162.98	162.98

Consequently,

$$K_{p,800} = \frac{(6.11)^2}{263.89} = 0.141468 \dots \text{ kPa} \approx \boxed{0.141 \text{ kPa}},$$

$$K_{p,1000} = \frac{(162.98)^2}{174.52} = 152.203 \dots \text{ kPa} \approx \boxed{152 \text{ kPa}}.$$

The dimensionless thermodynamic equilibrium constant includes a standard pressure:

$$K_{p,\text{dimensionless}} = \frac{(p_{\text{C}_2\text{H}_4}/p^\circ)(p_{\text{H}_2}/p^\circ)}{p_{\text{C}_2\text{H}_6}/p^\circ} = \frac{K_p}{p^\circ}.$$

For $p^\circ = 100 \text{ kPa}$, its values are 1.41×10^{-3} and 1.52 , respectively. Either convention gives the same ratio between temperatures.

4.5

The second equality sign in the printed van't Hoff equation must be replaced by multiplication. The dimensionally consistent equation is

$$\ln \frac{K_1}{K_2} = \frac{\overline{\Delta H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

Taking $T_1 = 1000 \text{ K}$ and $T_2 = 800 \text{ K}$,

$$\overline{\Delta H} = \frac{R \ln(K_{p,1000}/K_{p,800})}{1/800 - 1/1000}.$$

Using the unrounded equilibrium constants,

$$\ln \frac{152.203 \dots}{0.141468 \dots} = 6.98089,$$

and

$$\frac{1}{800} - \frac{1}{1000} = 2.50 \times 10^{-4} \text{ K}^{-1}.$$

Hence,

$$\overline{\Delta H} = \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(6.98089)}{2.50 \times 10^{-4} \text{ K}^{-1}} = 2.32157 \times 10^5 \text{ J mol}^{-1}.$$

Thus,

$$\boxed{\overline{\Delta H} \approx +232 \text{ kJ mol}^{-1}}.$$

The reaction is endothermic.

4.6

Increasing temperature favors the endothermic forward reaction and therefore increases the equilibrium conversion of ethane.

Increasing pressure by compression at constant temperature favors the side with fewer gas molecules. The reactant side contains one mole of gas per stoichiometric reaction, whereas the product side contains two; compression therefore decreases conversion.

This also follows from

$$K_p = \frac{\alpha^2 p}{1 - \alpha^2} \implies \alpha = \sqrt{\frac{K_p}{p + K_p}}.$$

At fixed temperature, K_p is constant, so increasing p decreases α .

In the stated experiment, heating a rigid vessel causes temperature, pressure and conversion to rise together; pressure is not independently increased by compression.

4.7

The problem does not identify which calculation's relative error is required. The directly available comparison is between the calculated and measured pressures.

Taking the measured pressure as the reference, define the magnitude of the relative discrepancy as

$$\boxed{\varepsilon_p = \frac{|p' - p|}{p} \times 100\%}.$$

If instead the requested quantity is the pressure excess relative to the calculated pressure, its denominator is p' . Both conventions give:

$T \text{ (K)}$	$\frac{ p' - p }{p} \times 100\%$	$\frac{ p - p' }{p'} \times 100\%$
300	0%	0%
500	0.266%	0.267%
800	2.21%	2.26%
1000	32.6%	48.3%

For example, at 1000 K,

$$\varepsilon_p = \frac{500.48 - 337.50}{500.48} \times 100\% = 32.5647 \dots \%$$

Under the assumed reaction model, the last column equals 100α . These discrepancies quantify the failure of the unchanged-composition pressure prediction. A numerical uncertainty or relative error in α , K_p , or $\overline{\Delta H}$ cannot be determined without measurement uncertainties or independent reference values.

The solution was checked against the official solution.

Problem 5: Liquid compound X from coal tar

A certain liquid organic compound **X** (being present in coal tar) with a mass of 1.06 g was burned to produce 0.90 g of water and 3.52 g of carbon dioxide. Its vapours were 3.79 times as dense as nitrogen.

The compound **X** was oxidised by a hot mixture of $\text{CrO}_3 + \text{H}_2\text{SO}_4$. A colourless crystalline substance **A** was isolated from the reaction mixture. It was soluble in an aqueous solution of NaOH or NaHCO_3 .

Compound **A** when heated loses water and converts to compound **B**. Condensation of compound **B** with phenol in the presence of H_2SO_4 or ZnCl_2 yields a substance **Y** which is very often used as an acid-base indicator.

Both compound **A** and compound **B** when heated with an excess of 1-butanol (some drops of a concentrated H_2SO_4 solution are added) gives the same liquid compound **C**.

If accepted that a carbon atom shows a tendency to form four bonds in organic compounds, it is possible to write formally two different formulas for the compound **X**. The formulas written in this way do not correspond, however, to the chemical structure of the molecule **X** because up to date nobody has succeeded in the preparation of the two hypothetical isomers.

Haayman and Witbaut carried out in 1941 an ozonisation of the compound **X** in a CH_3Cl solution. After hydrolysis of ozonides, it was found that the water layer contains three different organic compounds in a molar ratio of **D** : **E** : **F** = 3 : 2 : 1. Only two of them formed new compounds **G** and **H** by a mild oxidation, the third one remains unchanged under these conditions but the effect of stronger oxidising agents as H_2O_2 for example, results in forming a well known liquid compound **I** with a characteristic sharp smell.

A sample of a pure anhydrous compound **G** was dissolved in an aqueous 1-molar solution of H_2SO_4 and the resulting solution was titrated with a volumetric 0.05-molar KMnO_4 solution. An amount of 0.288 g of substance **G** required 25.6 cm^3 of the KMnO_4 solution.

Problems:

5.1 Write the summary formula for the compound **X**.

5.2 Based on the information and data in the task, write chemical equations for the reactions by which products **A**, **B**, and **C** are formed.

5.3 Give the name for compound **Y** and write the equation of its synthesis. Write its structural formula and colour in both acidic and basic solutions.

5.4 Write two formal structural formulas for the compound **X** as well as a more correct structural formula according to the latest findings.

5.5 Write the chemical equation for the ozonolysis of compound **X** by which the fact can be explained why compounds **D**, **E**, and **F** are after hydrolysis of ozonides present in water layer in a molar ration of 3 : 2 : 1.

5.6 Write chemical equations for the reactions of formation of compounds **G**, **H**, and **I**.

5.7 Write both formal structural formulas used before, and the more correct modern structural formula of another liquid organic compound if you know that the compound is also present in coal tar and it is a derivative of compound **X**. What name of a known chemist is connected in the history with the formula of this basic compound? What are the products obtained by its ozonolysis?

5.8 Write the names of the substances **X**, **Y**, **A – I** under the corresponding compounds in the equations.

Note:

Use in your calculation:

$$M(\text{C}) = 12 \text{ g mol}^{-1}; \quad M(\text{O}) = 16 \text{ g mol}^{-1}; \quad M(\text{H}) = 1 \text{ g mol}^{-1}; \quad M(\text{KMnO}_4) = 158 \text{ g mol}^{-1}.$$

Official English text of the problem.

Answers

- **5.1** $\boxed{\text{C}_8\text{H}_{10}}$. **X** is *o*-xylene, or 1,2-dimethylbenzene.
- **5.2** Oxidation gives **A**, **phthalic acid**; dehydration gives **B**, **phthalic anhydride**. Esterification of either with excess 1-butanol gives **C**, **di-*n*-butyl phthalate**.
- **5.3** **Y** is **phenolphthalein**, formed from one molecule of **B** and two molecules of phenol, with elimination of one molecule of water. Its neutral lactone is **colourless**; its quinoid dianion is **pink/magenta** in the usual basic indicator range.
- **5.4** With methyl groups at ring positions 1 and 2, the two formal Kekulé structures have double bonds at 1 = 2, 3 = 4, 5 = 6 and 2 = 3, 4 = 5, 6 = 1. The actual molecule has a delocalized aromatic ring.
- **5.5** **D** = **glyoxal**, **E** = **methylglyoxal**, **F** = **diacetyl**. The two formal cleavage patterns give $D + 2E$ and $2D + F$; equal contributions give $D : E : F = 3 : 2 : 1$.
- **5.6** **G** = **oxalic acid**, **H** = **pyruvic acid**, **I** = **acetic acid**. Mild oxidation converts **D** into **G** and **E** into **H**; peroxide cleavage of **F** produces two molecules of **I**. The titration confirms anhydrous oxalic acid, $M = 90 \text{ g mol}^{-1}$.
- **5.7** The intended parent compound is **benzene**, c1ccccc1, associated historically with **August Kekulé**. Its carbonyl-forming ozonolysis gives three molecules of glyoxal per molecule of benzene. The wording about the derivative relationship is reversed.
- **5.8** The complete identification key is:

Label	Name	SMILES
X	<i>o</i> -Xylene; 1,2-dimethylbenzene	<chem>Cc1ccccc1C</chem>
Y	Phenolphthalein, neutral lactone	<chem>O=C1OC(c2ccc(O)cc2)(c2ccc(O)cc2)c2ccccc21</chem>
A	Phthalic acid; benzene-1,2-dicarboxylic acid	<chem>O=C(O)c1ccccc1C(=O)O</chem>
B	Phthalic anhydride	<chem>O=C1OC(=O)c2ccccc21</chem>
C	Di- <i>n</i> -butyl phthalate	<chem>CCCCOC(=O)c1ccccc1C(=O)OCCCC</chem>

Label	Name	SMILES
D	Glyoxal; ethanedial	<chem>O=CC=O</chem>
E	Methylglyoxal; 2-oxopropanal	<chem>CC(=O)C=O</chem>
F	Diacetyl; butane-2,3-dione	<chem>CC(=O)C(=O)C</chem>
G	Oxalic acid; ethanedioic acid	<chem>O=C(O)C(=O)O</chem>
H	Pyruvic acid; 2-oxopropanoic acid	<chem>CC(=O)C(=O)O</chem>
I	Acetic acid; ethanoic acid	<chem>CC(=O)O</chem>

Solution

5.1 — Molecular formula of X

The combustion products give the amounts of carbon and hydrogen:

$$n(\text{C}) = n(\text{CO}_2) = \frac{3.52 \text{ g}}{44 \text{ g mol}^{-1}} = 0.0800 \text{ mol},$$

$$n(\text{H}) = 2n(\text{H}_2\text{O}) = 2 \frac{0.90 \text{ g}}{18 \text{ g mol}^{-1}} = 0.100 \text{ mol}.$$

The corresponding masses, retaining intermediate digits, are

$$m(\text{C}) = 0.960 \text{ g}, \quad m(\text{H}) = 0.100 \text{ g}.$$

Their sum equals the sample mass, 1.060 g. Thus the analysis accounts for the sample entirely as carbon and hydrogen.

The atomic ratio is

$$n(\text{C}) : n(\text{H}) = 0.0800 : 0.100 = 4 : 5,$$

so the empirical formula is C_4H_5 , with empirical formula mass

$$4(12) + 5(1) = 53 \text{ g mol}^{-1}.$$

At equal temperature and pressure, gas densities are proportional to molar masses. Taking $M(\text{N}_2) = 28 \text{ g mol}^{-1}$,

$$M(\text{X}) = 3.79(28) = 106.12 \text{ g mol}^{-1} \approx 106 \text{ g mol}^{-1}.$$

Consequently,

$$\frac{M(\text{X})}{M(\text{C}_4\text{H}_5)} \approx \frac{106}{53} = 2, \quad \boxed{\text{X} = \text{C}_8\text{H}_{10}}.$$

Its degree of unsaturation is

$$\frac{2(8) + 2 - 10}{2} = 4,$$

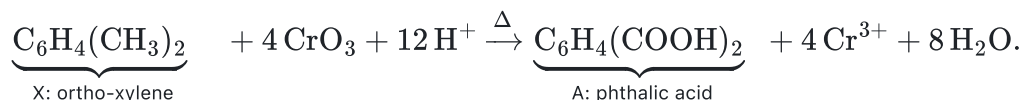
consistent with a benzene ring.

5.2 — Identification and formation of A, B, and C

Solubility in aqueous bicarbonate indicates an acidic compound, here a carboxylic acid. Formation of an anhydride on heating, followed by condensation with phenol to form an indicator, identifies the **phthalic acid–phthalic anhydride** pair.

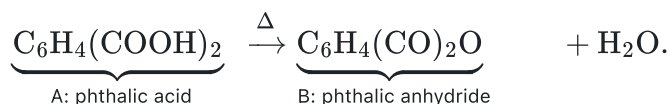
Phthalic acid has adjacent carboxyl groups and readily forms a five-membered cyclic anhydride. Therefore X must have adjacent methyl groups: it is ***o*-xylene**. Hot chromium(VI) oxidizes each methyl group to a carboxyl group.

A fully balanced equation in acidic solution is



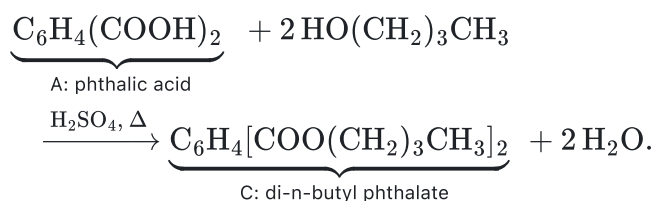
The two substituents in these condensed aromatic formulas occupy adjacent ring positions.

Heating A eliminates water:

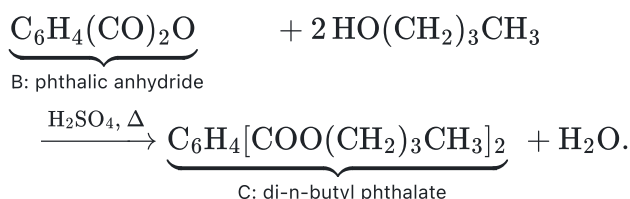


In B, the oxygen between the two acyl groups closes the five-membered anhydride ring fused to the benzene ring.

Excess **butan-1-ol**, CCCC, esterifies both carboxyl groups of A:

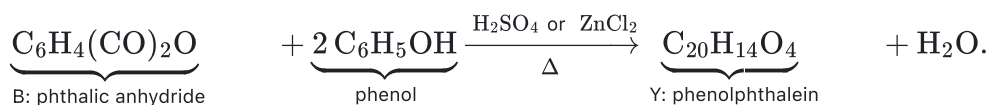


Starting with B gives the same diester, but only one net molecule of water is formed:



5.3 — Phenolphthalein: synthesis, structures, and colours

Phthalic anhydride condenses with two molecules of **phenol**, Oc1ccccc1, to form **phenolphthalein**:



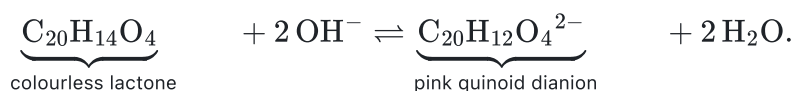
The relevant structures are:

Medium	Form, name, and colour	SMILES
Acidic	Neutral phenolphthalein lactone; colourless	<chem>O=C1OC(c2ccc(O)cc2)(c2ccc(O)cc2)c2ccccc21</chem>
Basic, usual indicator range	Phenolphthalein quinoid dianion; pink/magenta	<chem>O=C([O-])c1ccccc1C(c1ccc([O-])cc1)=C1C=CC(=O)C=C1</chem>

To draw the acidic structure, draw a phthalide ring whose tetrahedral carbon bears two **para-hydroxyphenyl** groups.

For the basic structure, open the lactone ring to give an **ortho-carboxylate** group. In the displayed resonance contributor, the central carbon is double-bonded to a quinonoid ring and single-bonded to a para-phenoxide ring. The charge and conjugation are delocalized; the single SMILES represents one contributor.

The overall acid–base conversion is



Ring opening and the resulting extended conjugation account for the visible colour. The stated basic colour refers to the normal indicator range; very strongly alkaline solutions can undergo further changes.

5.4 — Two formal structures and the aromatic structure of X

Number the ring carbons consecutively from 1 to 6, with methyl groups attached to positions 1 and 2.

Representation of <i>o</i> -xylene	Ring double bonds	SMILES
Kekulé contributor K_1	1 = 2, 3 = 4, 5 = 6	<chem>CC1=C(C)C=CC=C1</chem>
Kekulé contributor K_2	2 = 3, 4 = 5, 6 = 1	<chem>CC1C(C)=CC=CC=1</chem>
Delocalized aromatic structure	No fixed alternating localization	<chem>Cc1ccccc1C</chem>

In K_1 , the two methyl-bearing ring carbons share a formal double bond; in K_2 , they share a formal single bond.

For the modern drawing, draw a hexagon with an internal circle and methyl groups at two adjacent vertices. The aromatic ring is approximately planar, with six delocalized π electrons.

The Kekulé drawings are **resonance contributors, not separately existing isomers or molecules in equilibrium**. Their SMILES may therefore be converted to the same aromatic structure by chemical software.

5.5 — Ozonolysis and the 3 : 2 : 1 ratio

Formal ozonolytic cleavage converts each carbon of a localized double bond into a carbonyl carbon:

- A ring carbon bearing hydrogen becomes an aldehyde carbonyl.
- A ring carbon bearing a methyl group becomes a ketone carbonyl.

Cleaving the three formal double bonds leaves three two-carbon fragments, corresponding to the three remaining ring bonds.

Formal pattern	Remaining carbon pairs	Organic products
K_1 : cleave 1 = 2, 3 = 4, 5 = 6	2–3, 4–5, 6–1	One glyoxal D and two methylglyoxal E
K_2 : cleave 2 = 3, 4 = 5, 6 = 1	1–2, 3–4, 5–6	One diacetyl F and two glyoxal D

Thus one occurrence of each formal cleavage pattern gives

$$(D + 2E) + (2D + F) = 3D + 2E + F.$$

This reproduces the observed ratio:

$$\boxed{D : E : F = 3 : 2 : 1}.$$

Using the conventional formal balance for ozonide hydrolysis, with hydrogen peroxide as coproduct, the combined equation is



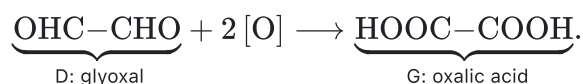
The solvent is **chloromethane**, CC1. Carbonyl products are written in their conventional unhydrated forms.

This is a formal cleavage account of the stipulated initial product mixture. It does not mean that X contains two independently existing Kekulé isomers, nor does resonance alone establish quantitative reaction branching.

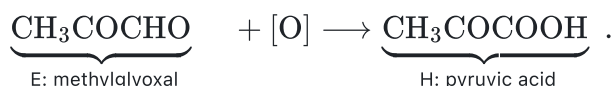
5.6 — Formation of G, H, and I; verification by titration

Here [O] denotes one oxygen equivalent supplied by an oxidizing reagent, rather than a free oxygen-atom intermediate.

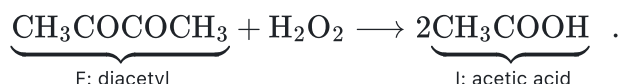
Mild oxidation converts both aldehyde groups of glyoxal into carboxyl groups:



Methylglyoxal has one aldehyde group and one ketone group. Oxidation of the aldehyde group gives pyruvic acid:

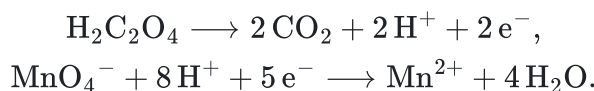


Diacetyl has two ketone groups and no aldehyde group, explaining its resistance to the stipulated mild oxidation. Hydrogen peroxide cleaves the bond between its carbonyl carbons:

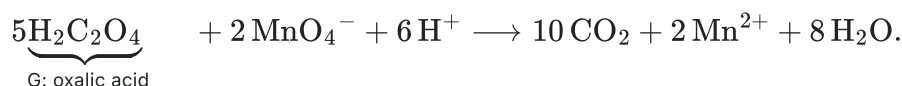


Acetic acid is the familiar liquid with a sharp, vinegar-like smell.

The titration independently checks the assignment of G. The relevant half-reactions are



Combining them gives



The amount of permanganate is

$$n(\text{MnO}_4^-) = 0.05 \text{ mol L}^{-1} \times 25.6 \times 10^{-3} \text{ L} = 1.28 \times 10^{-3} \text{ mol}.$$

From the 5 : 2 stoichiometry,

$$n(\text{G}) = \frac{5}{2} n(\text{MnO}_4^-) = 3.20 \times 10^{-3} \text{ mol}.$$

Hence the implied molar mass is

$$M(\text{G}) = \frac{0.288 \text{ g}}{3.20 \times 10^{-3} \text{ mol}} = 90 \text{ g mol}^{-1}.$$

For anhydrous oxalic acid,

$$M(\text{H}_2\text{C}_2\text{O}_4) = 2(1) + 2(12) + 4(16) = 90 \text{ g mol}^{-1},$$

exactly matching the titration data.

5.7 — Benzene, Kekulé structures, and ozonolysis

The intended basic or parent compound is **benzene**. More precisely, *o*-xylene is a dimethyl derivative of benzene.

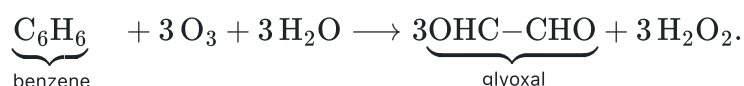
Using fixed numbering around a six-membered ring:

Benzene representation	Ring double bonds	SMILES
First Kekulé contributor	1 = 2, 3 = 4, 5 = 6	<chem>C1=CC=CC=C1</chem>
Second Kekulé contributor	2 = 3, 4 = 5, 6 = 1	<chem>C1C=CC=CC=1</chem>
Aromatic structure	Six delocalized π electrons	<chem>c1ccccc1</chem>

The corresponding drawings are two hexagons with alternating double bonds shifted by one edge, and a modern hexagon containing a circle. Every ring carbon bears one hydrogen. Benzene is planar and all six carbon–carbon bonds are equivalent.

The historical chemist is **August Kekulé**.

Because every ring carbon bears hydrogen, either formal cleavage pattern produces only glyoxal as the organic carbonyl product. The conventional hydrolysis balance is



Thus one molecule of benzene gives **three molecules of glyoxal** under the carbonyl-forming work-up considered here.

5.8 — Names beneath the formulas and remaining SMILES

The names of X, Y, and A–I appear beneath their formulas in the equations above; their complete name–SMILES key is given in Answers 5.8.

For completeness, the other molecular and ionic species used in the solution are:

Species	SMILES
Water	<chem>O</chem>
Carbon dioxide	<chem>O=C=O</chem>
Dinitrogen	<chem>N#N</chem>
Ozone	<chem>[O-][O+]=O</chem>
Hydrogen peroxide	<chem>OO</chem>
Sulfuric acid	<chem>OS(=O)(=O)O</chem>
Chromium(VI) oxide	<chem>O=[Cr](=O)=O</chem>
Chromium(III) ion	<chem>[Cr+3]</chem>
Hydrogen ion	<chem>[H+]</chem>
Hydroxide ion	<chem>[OH-]</chem>
Sodium hydroxide	<chem>[Na+] . [OH-]</chem>
Sodium hydrogen carbonate	<chem>[Na+] . OC(=O)[O-]</chem>
Zinc chloride	<chem>[Zn+2] . [Cl-] . [Cl-]</chem>
Potassium permanganate	<chem>[K+] . [O-][Mn](=O)(=O)=O</chem>
Permanganate ion	<chem>[O-][Mn](=O)(=O)=O</chem>
Manganese(II) ion	<chem>[Mn+2]</chem>

The disconnected salt SMILES specify ionic composition; they do not specify solvation or solid-state coordination.

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.