

IChO 1975

Theory problems and solutions · Veszprém, Hungary · 8 theory problems with complete solutions

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Problem 1: Crystallisation of alum on evaporation

How many grams of alum $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ are crystallised out from 320 g $\text{KAl}(\text{SO}_4)_2$ solution saturated at 20 °C if 160 g of water are evaporated from the solution at 20 °C?

(The solution saturated at 20 °C contains 5.50 % of $\text{KAl}(\text{SO}_4)_2$ by mass.)

Relative atomic masses:

$A_r(\text{K}) = 39.10$; $A_r(\text{Al}) = 26.98$; $A_r(\text{S}) = 32.06$; $A_r(\text{O}) = 16.0$; $A_r(\text{H}) = 1.01$

Official English text of the problem.

Answers

1. 18.0 g of potassium alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, crystallises out.

Solution

1. Potassium alum is potassium aluminium sulfate dodecahydrate. Its stoichiometric, disconnected SMILES is [K+] . [Al+3] . [O-]S(=O)(=O)[O-] . [O-]S(=O)(=O)[O-] . O.O.O.O.O.O.O.O.O.O.O.O.O.O. This represents its composition; it does not specify the crystal lattice or coordination geometry. Water, H_2O , has SMILES O.

The molar masses calculated from the supplied atomic masses are

$$\begin{aligned} M(\text{KAl}(\text{SO}_4)_2) &= 39.10 + 26.98 + 2(32.06 + 4 \times 16.0) \\ &= 258.20 \text{ g mol}^{-1}, \\ M(\text{H}_2\text{O}) &= 2(1.01) + 16.0 = 18.02 \text{ g mol}^{-1}, \\ M(\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}) &= 258.20 + 12(18.02) \\ &= 474.44 \text{ g mol}^{-1}. \end{aligned}$$

Thus the mass fraction of anhydrous $\text{KAl}(\text{SO}_4)_2$ in the crystals is

$$f = \frac{258.20}{474.44}.$$

Initially, the solution contains

$$m_0(\text{KAl}(\text{SO}_4)_2) = 0.0550(320 \text{ g}) = 17.60 \text{ g}.$$

Let x be the mass of hydrated crystals formed. Evaporation removes 160 g of water, and crystallisation removes x from the liquid, so the remaining solution has mass

$$m_{\text{solution}} = 320 \text{ g} - 160 \text{ g} - x = 160 \text{ g} - x.$$

The crystals remove $\frac{258.20}{474.44}x$ of anhydrous salt, together with their water of crystallisation. Since the remaining solution is saturated at 20 °C, its salt mass fraction is still 0.0550. Therefore,

$$17.60 \text{ g} - \frac{258.20}{474.44}x = 0.0550(160 \text{ g} - x).$$

Solving,

$$x = \frac{17.60 \text{ g} - 0.0550(160 \text{ g})}{\frac{258.20}{474.44} - 0.0550} = 17.99 \text{ g} \approx \boxed{18.0 \text{ g}}.$$

The solution was checked against the official solution.

Problem 2: Composition of an Al-Zn-Si-Cu alloy

An alloy prepared for experimental purposes contains aluminium, zinc, silicon, and copper. If 1000 mg of the alloy are dissolved in hydrochloric acid, 843 cm³ of hydrogen (0 °C, 101.325 kPa) are evolved and 170 mg of an undissolved residue remain. A sample of 500 mg of the alloy when reacted with a NaOH solution produces 517 cm³ of hydrogen at the above conditions and in this case remains also an undissolved fraction.

Problem:

2.1 Calculate the composition of the alloy in % by mass.

Relative atomic masses:

$$A_r(\text{Al}) = 26.98; \quad A_r(\text{Zn}) = 65.37; \quad A_r(\text{Si}) = 28.09; \quad A_r(\text{Cu}) = 63.55.$$

Official English text of the problem.

Answers

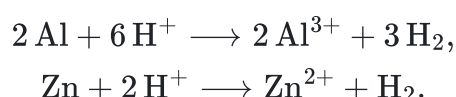
- 2.1** The alloy contains approximately **61.8% aluminium, 21.2% zinc, 12.0% silicon, and 5.0% copper by mass.**

Solution

2.1

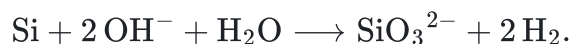
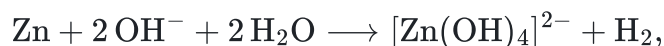
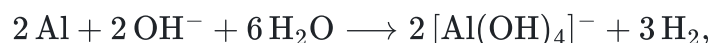
Aluminium and zinc dissolve in hydrochloric acid and release hydrogen. Silicon and copper remain undissolved, so the 170 mg acid residue consists of these two elements.

The balanced net ionic reactions are



The species are hydrogen ions $[H^+]$, aluminium(III) ions $[Al^{3+}]$, zinc(II) ions $[Zn^{2+}]$, and hydrogen $[H_2]$.

In sodium hydroxide solution, aluminium and zinc dissolve because of their amphoteric behaviour; silicon also reacts, releasing hydrogen. Copper remains undissolved. The balanced equations are



Here hydroxide is $[OH^-]$ and water is O . The products are tetrahydroxoaluminate(III), $[Al(OH)_4]^-$; tetrahydroxozincate(II), $[Zn(OH)_4]^{2-}$; and formally metasilicate, $[SiO_3]^{2-}$. The two hydroxo complexes have tetrahedral metal centres, which these SMILES do not specify. The silicon equation uses the conventional metasilicate representation; aqueous hydration and speciation do not change the hydrogen yield.

Thus, each mole of aluminium produces $3/2$ mol of hydrogen in either medium, each mole of zinc produces 1 mol, and each mole of silicon produces 2 mol in alkali only.

Use a **1.000 g alloy basis** and the molar gas volume at the stated conditions,

$$V_m = 22.414 \text{ dm}^3 \text{ mol}^{-1}.$$

The alkaline experiment, scaled from 500 mg to 1000 mg of alloy, would produce

$$V_{\text{alkali}} = 2(517) = 1034 \text{ cm}^3.$$

Because aluminium and zinc produce the same amounts of hydrogen in both media, the excess is entirely attributable to silicon:

$$\Delta V = 1034 - 843 = 191 \text{ cm}^3 = 0.191 \text{ dm}^3.$$

Consequently,

$$n_{\text{Si}} = \frac{\Delta V}{2V_m} = \frac{0.191}{2(22.414)} = 4.26073 \times 10^{-3} \text{ mol},$$

$$m_{\text{Si}} = n_{\text{Si}} M_{\text{Si}} = (4.26073 \times 10^{-3})(28.09) = 0.119684 \text{ g}.$$

The remainder of the acid residue is copper:

$$m_{\text{Cu}} = 0.170 - 0.119684 = 0.050316 \text{ g}.$$

The total mass of aluminium and zinc is therefore

$$m_{\text{Al}} + m_{\text{Zn}} = 1.000 - 0.170 = 0.830 \text{ g}.$$

The acid hydrogen yield gives a second equation:

$$\frac{3}{2} \frac{m_{\text{Al}}}{26.98 \text{ g mol}^{-1}} + \frac{m_{\text{Zn}}}{65.37 \text{ g mol}^{-1}} = \frac{0.843 \text{ dm}^3}{22.414 \text{ dm}^3 \text{ mol}^{-1}} = 0.0376104 \text{ mol}.$$

Substituting $m_{\text{Zn}} = 0.830 \text{ g} - m_{\text{Al}}$ and solving gives

$$m_{\text{Al}} = 0.618212 \text{ g}, \quad m_{\text{Zn}} = 0.211788 \text{ g}.$$

Finally,

$$w_i = 100 \frac{m_i}{1.000 \text{ g}},$$

so the composition, rounded to 0.1 percentage point, is

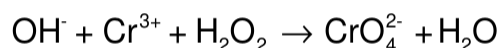
Element	Percentage by mass
Aluminium	61.8%
Zinc	21.2%
Silicon	12.0%
Copper	5.0%
Total	100.0%

The solution was checked against the official solution.

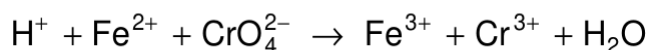
Problem 3: Composition of an Ag-Cu-Cr alloy

A sample of 1500 mg of an alloy that contains silver, copper, and chromium is dissolved and the solution containing Ag^+ , Cu^{2+} , and Cr^{3+} ions, is diluted to exactly 500 cm^3 . One tenth of the volume of that solution is taken for further procedure:

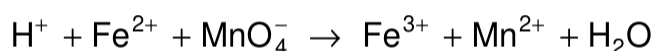
After elimination of silver and copper, chromium is oxidised in it according to the following unbalanced equation:



Then 25.00 cm^3 of a 0.100 molar Fe(II) salt solution are added. The following reaction (written in an unbalanced form) is taking place:



According to the unbalanced equation:



a volume of 17.20 cm^3 of a 0.020-molar KMnO_4 solution is required for an oxidation of the Fe(II) salt which remains unoxidized in the solution.

In another experiment, a volume of 200 cm^3 of the initial solution is electrolysed. Due to secondary reactions, the efficiency of the electrolysis is 90 % for metals under consideration. All three metals are quantitatively deposited in 14.50 minutes by passing a current of 2 A through the solution.

Problem:

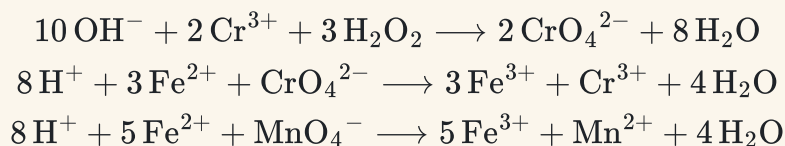
3.1 Balance the three chemical equations and calculate the composition of the alloy in % by mass.

Relative atomic masses: $A_r(\text{Cu}) = 63.55$; $A_r(\text{Ag}) = 107.87$; $A_r(\text{Cr}) = 52.00$

Official English text of the problem.

Answers

- 3.1 The balanced equations are:



The alloy composition by mass is:

Silver: 30.6%,	Copper: 60.4%,	Chromium: 9.0%.
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Solution

3.1 — Balancing the reactions

In the first reaction, chromium is oxidised from oxidation state +3 to +6, losing three electrons per chromium atom. Hydrogen peroxide accepts two electrons per molecule as its oxygen changes from oxidation state -1 to -2 . Thus, two chromium ions react with three hydrogen peroxide molecules. Balancing oxygen, hydrogen, and charge in alkaline solution gives:



In the second reaction, chromium is reduced from +6 to +3, accepting three electrons, while each iron(II) ion loses one electron. Consequently, one chromate ion consumes three iron(II) ions:



In the third reaction, manganese is reduced from +7 to +2, accepting five electrons. One permanganate ion therefore oxidises five iron(II) ions:



Chromium content from the back titration

The analysed aliquot has volume

$$V_{\text{aliquot}} = \frac{500}{10} = 50.0 \text{ cm}^3.$$

Keeping guard digits until the final percentages, the amount of iron(II) initially added is

$$n_{\text{Fe,added}} = (25.00 \times 10^{-3} \text{ L})(0.100 \text{ mol L}^{-1}) = 2.500 \times 10^{-3} \text{ mol}.$$

The amount of permanganate used in the back titration is

$$n_{\text{permanganate}} = (17.20 \times 10^{-3} \text{ L})(0.020 \text{ mol L}^{-1}) = 3.440 \times 10^{-4} \text{ mol}.$$

Since each permanganate ion consumes five iron(II) ions, the remaining iron(II) amounted to

$$n_{\text{Fe,remaining}} = 5(3.440 \times 10^{-4}) = 1.720 \times 10^{-3} \text{ mol}.$$

Hence the amount consumed by chromate was

$$n_{\text{Fe,consumed}} = 2.500 \times 10^{-3} - 1.720 \times 10^{-3} = 7.80 \times 10^{-4} \text{ mol}.$$

Three iron(II) ions reduce one chromate ion, so the chromium content of the aliquot is

$$n_{\text{Cr,aliquot}} = \frac{7.80 \times 10^{-4}}{3} = 2.60 \times 10^{-4} \text{ mol}.$$

The entire sample therefore contains

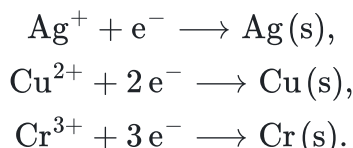
$$n_{\text{Cr}} = 10n_{\text{Cr,aliquot}} = 2.60 \times 10^{-3} \text{ mol},$$
$$m_{\text{Cr}} = (2.60 \times 10^{-3} \text{ mol})(52.00 \text{ g mol}^{-1}) = 0.1352 \text{ g}.$$

Thus,

$$w_{\text{Cr}} = \frac{0.1352}{1.500} \times 100\% = 9.0133 \dots \%$$

Silver and copper contents from electrolysis

The cathodic deposition reactions are



Thus, depositing one mole of silver, copper, or chromium requires respectively one, two, or three moles of electrons.

The total charge passed is

$$Q = It = (2 \text{ A})(14.50 \times 60 \text{ s}) = 1740 \text{ C}.$$

Only 90% of this charge deposits the metals:

$$Q_{\text{metals}} = 0.90(1740) = 1566 \text{ C}.$$

Using the standard Faraday constant $F = 96485 \text{ C mol}^{-1}$, the electron amount used for deposition from the 200 cm^3 portion is

$$n_{e,200} = \frac{1566}{96485} = 0.0162305 \text{ mol}.$$

Let n_{Ag} , n_{Cu} , and n_{Cr} denote the metal amounts in the **entire original sample**. Scaling from 200 to 500 cm^3 ,

$$n_{\text{Ag}} + 2n_{\text{Cu}} + 3n_{\text{Cr}} = \frac{500}{200}(0.0162305) = 0.0405763 \text{ mol}.$$

Substituting the chromium amount gives

$$n_{\text{Ag}} + 2n_{\text{Cu}} = 0.0405763 - 3(0.002600) = 0.0327763 \text{ mol}.$$

The silver and copper together have mass

$$m_{\text{Ag}} + m_{\text{Cu}} = 1.500 - 0.1352 = 1.3648 \text{ g}.$$

Their mass equation is therefore

$$(107.87 \text{ g mol}^{-1})n_{\text{Ag}} + (63.55 \text{ g mol}^{-1})n_{\text{Cu}} = 1.3648 \text{ g}.$$

Substituting $n_{\text{Ag}} = 0.0327763 \text{ mol} - 2n_{\text{Cu}}$ and solving gives

$$n_{\text{Cu}} \approx 0.0142636 \text{ mol}, \quad n_{\text{Ag}} \approx 0.00424909 \text{ mol}.$$

Consequently,

$$m_{\text{Cu}} \approx 0.906451 \text{ g}, \quad m_{\text{Ag}} \approx 0.458349 \text{ g}.$$

The mass percentages are

$$w_{\text{Ag}} = \frac{0.458349}{1.500} \times 100\% \approx \boxed{30.6\%},$$

$$w_{\text{Cu}} = \frac{0.906451}{1.500} \times 100\% \approx \boxed{60.4\%},$$

$$w_{\text{Cr}} \approx \boxed{9.0\%}.$$

The calculated masses sum to 1.500 g, and the reported percentages sum to 100.0%.

Species names and SMILES

Species	Name	SMILES
Ag^+	Silver(I) ion	[Ag+]
Cu^{2+}	Copper(II) ion	[Cu+2]
Cr^{3+}	Chromium(III) ion	[Cr+3]
OH^-	Hydroxide ion	[OH-]
H_2O_2	Hydrogen peroxide	OO
CrO_4^{2-}	Chromate ion	[O-][Cr](=O)(=O)[O-]
H_2O	Water	O
H^+	Hydrogen ion (proton)	[H+]
Fe^{2+}	Iron(II) ion	[Fe+2]
Fe^{3+}	Iron(III) ion	[Fe+3]
MnO_4^-	Permanganate ion	[O-][Mn](=O)(=O)=O
Mn^{2+}	Manganese(II) ion	[Mn+2]
KMnO_4	Potassium permanganate	[K+]·[O-][Mn](=O)(=O)=O

The ion SMILES omit aqueous solvation. Chromate and permanganate have tetrahedral oxygen arrangements; these SMILES do not specify that geometry and show only one formal representation of their delocalized bonding.

The solution was checked against the official solution.

Problem 4: Dilution of formic acid and degree of ionisation

The pH value of a solution containing 3 % by mass of formic acid ($\rho = 1.0049 \text{ g cm}^{-3}$) is equal to 1.97.

Problem:

4.1 How many times should the solution be diluted to attain a tenfold increase in the value of ionisation degree?

Relative atomic masses: $A_r(\text{H}) = 1.01$; $A_r(\text{C}) = 12.01$; $A_r(\text{O}) = 16$.

Official English text of the problem.

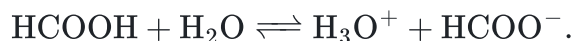
Answers

- **4.1:** The required dilution factor is $117.6 \approx 118$: the final solution volume should be approximately **118 times the initial volume**.

Solution

4.1

Formic acid $\text{O}=\text{CO}$ reacts with water O to form hydronium $[\text{OH}_3^+]$ and formate $\text{O}=\text{C}[\text{O}^-]$:



We use the usual approximation of concentrations for activities and neglect the autoionisation of water.

The molar mass of formic acid is

$$M = 2(1.01) + 12.01 + 2(16) = 46.03 \text{ g mol}^{-1}.$$

One litre of the initial solution has mass

$$m_{\text{solution}} = (1000 \text{ cm}^3)(1.0049 \text{ g cm}^{-3}) = 1004.9 \text{ g},$$

and therefore contains $0.03(1004.9) = 30.147 \text{ g}$ of formic acid. Its analytical concentration is

$$c_1 = \frac{30.147 \text{ g}}{(46.03 \text{ g mol}^{-1})(1 \text{ L})} = 0.654942 \text{ mol L}^{-1}.$$

The initial hydronium concentration follows from the pH:

$$[\text{H}_3\text{O}^+]_1 = 10^{-1.97} \text{ mol L}^{-1} = 0.0107152 \text{ mol L}^{-1}.$$

Consequently, the initial degree of ionisation is

$$\alpha_1 = \frac{[\text{H}_3\text{O}^+]_1}{c_1} = \frac{0.0107152}{0.654942} = 0.0163605.$$

The required final degree is thus

$$\alpha_2 = 10\alpha_1 = 0.163605.$$

For an analytical acid concentration c and degree of ionisation α ,

$$[\text{H}_3\text{O}^+] = [\text{HCOO}^-] = c\alpha, \quad [\text{HCOOH}] = c(1 - \alpha).$$

Hence the concentration form of the acid dissociation constant is

$$K_a = \frac{c\alpha^2}{1 - \alpha}.$$

At constant temperature, this gives for the two solutions

$$\frac{c_1\alpha_1^2}{1 - \alpha_1} = \frac{c_2(10\alpha_1)^2}{1 - 10\alpha_1}.$$

Cancelling α_1^2 and rearranging explicitly,

$$c_1(1 - 10\alpha_1) = 100c_2(1 - \alpha_1),$$

so

$$\frac{c_1}{c_2} = 100 \frac{1 - \alpha_1}{1 - 10\alpha_1}.$$

Dilution conserves the total amount of acid, so $c_1 V_1 = c_2 V_2$. Therefore,

$$\frac{V_2}{V_1} = \frac{c_1}{c_2} = 100 \frac{1 - 0.0163605}{1 - 0.163605} = 117.6047 \approx 118.$$

The $1 - \alpha$ factors must be retained because the final ionisation degree is about 16.4%; the small-ionisation approximation would give an inaccurate dilution factor of 100.

The solution was checked against the official solution.

Problem 5: Two consecutive aldehydes of a homologous series

A certain aldehyde **B** is subsequent to an aldehyde **A** in the homologous series of aldehydes. An amount of 19 g of aldehyde **B** is added to 100 g of an aqueous solution containing 23 mass % of aldehyde **A**. Addition of AgNO_3 in ammonia solution to 2 g of the aldehydes solution results in a precipitation of 4.35 g of silver.

Problems:

5.1 Determine by calculation what aldehydes were used.

5.2 Give the structural formulas of the aldehydes.

Relative atomic masses:

$$A_r(\text{C}) = 12.01; \quad A_r(\text{O}) = 16.00; \quad A_r(\text{H}) = 1.01; \quad A_r(\text{Ag}) = 107.87$$

Official English text of the problem.

Answers

- **5.1** Taking oxidation to stop at the carboxylate, **A** is **methanal (formaldehyde)**, C=O , and **B** is **ethanal (acetaldehyde)**, CC=O .
- **5.2** Methanal: $\text{H}-\text{C}(=\text{O})-\text{H}$, C=O . Ethanal: $\text{CH}_3-\text{C}(=\text{O})-\text{H}$, CC=O .

Solution

5.1 Identification by calculation

The final solution contains

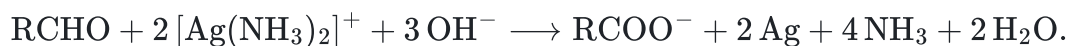
$$m_A = 100 \text{ g} \times 0.23 = 23 \text{ g}, \quad m_B = 19 \text{ g},$$

and its total mass is

$$m_{\text{solution}} = 100 + 19 = 119 \text{ g}.$$

The analysed portion therefore contains $2/119$ of each aldehyde.

Oxidation of an aldehyde to its carboxylate by ammoniacal silver(I) is represented by



At this endpoint, **one mole of aldehyde produces two moles of silver.**

The silver obtained corresponds to

$$n(\text{Ag}) = \frac{4.35 \text{ g}}{107.87 \text{ g mol}^{-1}} = 0.0403263 \text{ mol}.$$

Thus the total amount of aldehydes in the analysed portion is

$$n_A + n_B = \frac{0.0403263}{2} = 0.0201632 \text{ mol}.$$

Consecutive members of the saturated, acyclic monoaldehyde series differ by CH_2 , so

$$M_B - M_A = 12.01 + 2(1.01) = 14.03 \text{ g mol}^{-1}.$$

Consequently,

$$\frac{2 \text{ g}}{119 \text{ g}} \left[\frac{23 \text{ g}}{M_A} + \frac{19 \text{ g}}{M_A + 14.03 \text{ g mol}^{-1}} \right] = 0.0201632 \text{ mol}.$$

Solving this equation and retaining the positive root gives

$$M_A = 29.957 \text{ g mol}^{-1}, \quad M_B = 43.987 \text{ g mol}^{-1}.$$

The general molecular formula is $\text{C}_n\text{H}_{2n}\text{O}$, with

$$M_n = (14.03n + 16.00) \text{ g mol}^{-1}.$$

For A,

$$n = \frac{29.957 - 16.00}{14.03} = 0.9948 \approx 1.$$

Therefore A has one carbon atom and B has two:

- **A:** CH_2O , methanal (formaldehyde), $\text{C}=\text{O}$; $M_A = 30.03 \text{ g mol}^{-1}$.
- **B:** $\text{C}_2\text{H}_4\text{O}$, ethanal (acetaldehyde), $\text{CC}=\text{O}$; $M_B = 44.06 \text{ g mol}^{-1}$.

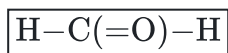
Using these formula masses to check the silver yield,

$$m(\text{Ag}) = \frac{2}{119} \left(\frac{23}{30.03} + \frac{19}{44.06} \right) (2)(107.87) \text{ g} = 4.3407 \text{ g}.$$

This is close to the stated 4.35 g.

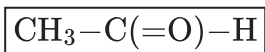
5.2 Structural formulas

A — methanal (formaldehyde), $\text{C}=\text{O}$:



Its carbonyl carbon is double bonded to oxygen and singly bonded to two hydrogen atoms.

B — ethanal (acetaldehyde), $\text{CC}=\text{O}$:

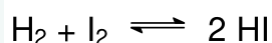


Its carbonyl carbon is double bonded to oxygen and singly bonded to one hydrogen atom and one methyl group.

The solution was checked against the official solution.

Problem 6: Hydrogen iodide equilibrium at 600 °C

The equilibrium constant of the reaction



is at 600 °C equal to 70.0.

Problems:

6.1 How much iodine (in %) is converted till the equilibrium is reached if the reactants are mixed in:

a) 1 : 1 molar ratio at 600 °C;

b) 2 : 1 molar ratio at 600 °C (the amount of hydrogen is twice as great as that of iodine).

6.2 How many moles of hydrogen should be mixed with one mole of iodine when 99 % of iodine is to be converted to hydrogen iodide till the equilibrium is reached at 600 °C?

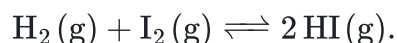
Official English text of the problem.

Answers

- **6.1 a)** 80.7% of the iodine is converted.
- **6.1 b)** 95.1% of the iodine is converted.
- **6.2** Initially mix 6.59 mol of hydrogen with one mole of iodine.

Solution

The balanced equilibrium reaction is



The species are hydrogen, H_2 , $[\text{H}][\text{H}]$; iodine, I_2 , $[\text{I}][\text{I}]$; and hydrogen iodide, HI , $[\text{H}][\text{I}]$.

Take an initial amount of 1.00 mol of iodine and r mol of hydrogen, with no hydrogen iodide initially.

Let x be the fraction of the initial iodine converted.

Species	Initial amount / mol	Equilibrium amount / mol
H_2	r	$r - x$
I_2	1	$1 - x$
HI	0	$2x$

At 600 °C,

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 70.0.$$

The volume factors cancel because the total stoichiometric coefficients are equal on both sides:

$$70.0 = \frac{(2x/V)^2}{((r-x)/V)((1-x)/V)} = \frac{4x^2}{(r-x)(1-x)}.$$

6.1 a) Initial molar ratio 1 : 1

Here $r = 1$, so

$$70.0 = \frac{4x^2}{(1-x)^2}.$$

Since $0 < x < 1$, taking the positive square root gives

$$\sqrt{70.0} = \frac{2x}{1-x}, \quad x = \frac{\sqrt{70.0}}{2 + \sqrt{70.0}} = 0.807073.$$

Therefore,

Iodine conversion = 80.7%.

6.1 b) Initial molar ratio 2 : 1

Here $r = 2$:

$$70.0 = \frac{4x^2}{(2-x)(1-x)}.$$

Rearranging,

$$\begin{aligned} 70(2 - 3x + x^2) &= 4x^2, \\ 33x^2 - 105x + 70 &= 0. \end{aligned}$$

Thus,

$$x = \frac{105 \pm \sqrt{1785}}{66}.$$

The larger root, 2.23105, is impossible because the iodine conversion cannot exceed 1. The physical root is

$$x = \frac{105 - \sqrt{1785}}{66} = 0.950769.$$

Therefore,

Iodine conversion = 95.1%.

6.2 Hydrogen required for 99% iodine conversion

Set $x = 0.99$. With one mole of iodine initially, the equilibrium amounts are

$$n(\text{I}_2) = 0.01 \text{ mol}, \quad n(\text{HI}) = 1.98 \text{ mol}, \quad n(\text{H}_2) = (r - 0.99) \text{ mol}.$$

Hence,

$$70.0 = \frac{1.98^2}{(r - 0.99)(0.01)}.$$

Solving for the initial hydrogen amount,

$$r = 0.99 + \frac{1.98^2}{70.0(0.01)} = 6.59057.$$

Therefore,

$$n_0(\text{H}_2) = 6.59 \text{ mol per 1 mol of iodine.}$$

Of this hydrogen, 0.99 mol reacts and approximately 5.60 mol remains at equilibrium.

The solution was checked against the official solution.

Problem 7: Oxidation products of a saturated hydrocarbon

A certain saturated hydrocarbon **A** is transformed by a catalytic oxidation partly into a secondary alcohol **B**, and partly into a ketone **C**. The ketone when oxidised with nitric acid in the presence of catalyst yields a compound **D** with a formula of $\text{C}_6\text{H}_{10}\text{O}_4$. From compound **D** when heated in the presence of acetic anhydride, a ketone **E** is formed, its formation being accompanied by evolution of CO_2 and H_2O . Compounds **E** and **C** have similar structures but compound **E** contains one methylene group less than ketone **C**. Compound **D** is one of the starting materials in the production of an important polycondensation synthetic fibre.

Problem:

7.1 Write the structural formulas of compounds **A**, **B**, **C**, **D**, and **E**.

Official English text of the problem.

Answers

- 7.1:** The compounds are:

Compound	Name	Structural description	SMILES
A	Cyclohexane	Six-membered ring of methylene groups	<chem>C1CCCCC1</chem>
B	Cyclohexanol	Six-membered carbon ring with one $\text{CH}(\text{OH})$ group and five methylene groups	<chem>OC1CCCCC1</chem>
C	Cyclohexanone	Six-membered ring containing one carbonyl carbon and five methylene groups	<chem>O=C1CCCCC1</chem>
D	Adipic acid (hexanedioic acid)	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$	<chem>O=C(O)CCCC(=O)O</chem>
E	Cyclopentanone	Five-membered ring containing one carbonyl carbon and four methylene groups	<chem>O=C1CCCC1</chem>

Solution

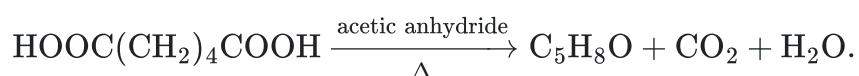
7.1

The fibre-production clue identifies **D** as **adipic acid**, a monomer used to manufacture nylon-6,6. Its structure, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, has exactly the required molecular formula $\text{C}_6\text{H}_{10}\text{O}_4$. Its two degrees of unsaturation,

$$\text{DBE} = \frac{2(6) + 2 - 10}{2} = 2,$$

are accounted for by the two carboxyl carbonyl groups.

On heating in the presence of **acetic anhydride**, $\text{CC}(=\text{O})\text{OC}(\text{C})=\text{O}$, adipic acid undergoes intramolecular ketonic decarboxylation. The four methylene carbons and one carboxyl carbon form a five-membered ketone ring; the remaining carboxyl carbon is lost as **carbon dioxide**, $\text{O}=\text{C}=\text{O}$. The balanced net reaction also produces **water**, O :



Thus **E** is **cyclopentanone**.

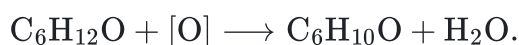
Since **C** has a similar structure but contains one additional methylene group, **C must be cyclohexanone**. Its six-membered ring contains five methylene groups and one carbonyl carbon, whereas cyclopentanone contains four methylene groups and one carbonyl carbon.

Oxidation of cyclohexanone with **nitric acid**, $\text{O}=[\text{N}^+](\text{O}^-)\text{O}$, cleaves a carbon-carbon bond adjacent to the carbonyl group and opens the ring to give adipic acid:

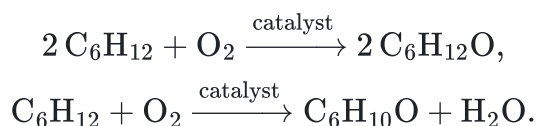


Here $[\text{O}]$ represents a formal oxygen-atom equivalent supplied by the oxidant. This balanced oxidation equation leaves the nitrogen-containing reduction products unspecified, as in the problem.

The corresponding secondary alcohol **B** is therefore **cyclohexanol**. The carbon bearing its hydroxyl group is bonded to two other carbon atoms, making it a secondary alcohol. Oxidation of this group gives the ketone:



Finally, the saturated hydrocarbon retaining this six-membered carbon skeleton is **cyclohexane**, **A**. Its catalytic oxidation with **oxygen**, $\text{O}=\text{O}$, gives cyclohexanol and cyclohexanone through the following balanced overall reactions:



All five structures therefore satisfy the oxidation sequence, the loss of one methylene group between **C** and **E**, and the synthetic-fibre clue.

The solution was checked against the official solution.

Problem 8: Molecular properties table and isoelectronic species

a) Mark by the "+" in a corresponding window those molecules for which the assertions written on the left side of the Table, are true.

Assertion	Molecule			
	C ₂ H ₄	N ₂ H ₄	H ₂ O ₂	H ₂ F ₂
There is a covalent bond between two equal atoms				
The molecule contains a double bond				
The molecule is planar				
The molecule is polar				
There is also a hydrogen bond in the molecule				
It has basic properties in relation to water				

b) The following assertion and Table are incomplete. Fill in the dotted places by a missing word and the missing formulas, respectively.

Assertion: The electronic structures of the molecules (ions) being placed in the Table one under the other are

CH ₄	C ₂ H ₆	CO ₃ ²⁻		C ₂ O ₄ ²⁻	
NH ₄ ⁺	N ₂ H ₆ ²⁺		NO ₂ ⁺		N ₂

Official English text of the problem.

Answers

- a) Place the "+" signs as follows. Empty cells indicate false assertions.

Assertion	C ₂ H ₄	N ₂ H ₄	H ₂ O ₂	H ₂ F ₂
There is a covalent bond between two equal atoms	+	+	+	
The molecule contains a double bond	+			
The molecule is planar	+			+
The molecule is polar		+	+	+
There is also a hydrogen bond in the molecule				+
It has basic properties in relation to water		+		

- b) Missing word: **identical**, in the intended sense that the corresponding species are **isoelectronic**, with analogous Lewis-electron structures.

One consistent completion is:

CH ₄	C ₂ H ₆	CO ₃ ²⁻	CO ₂	C ₂ O ₄ ²⁻	C ₂ ²⁻
NH ₄ ⁺	N ₂ H ₆ ²⁺	NO ₃ ⁻	NO ₂ ⁺	N ₂ O ₄	N ₂

Carbon monoxide, CO, is also a valid answer for the final blank.

Solution

a)

The structures represented by the four formulas are:

Species	Name	SMILES	Relevant structure
C ₂ H ₄	Ethene (ethylene)	C=C	Two trigonal-planar carbon atoms joined by a double bond; all six atoms are coplanar.
N ₂ H ₄	Hydrazine	NN	A single nitrogen–nitrogen bond; each nitrogen is pyramidal. The equilibrium conformation is nonplanar and gauche.
H ₂ O ₂	Hydrogen peroxide	OO	A single oxygen–oxygen bond and a nonplanar, skew equilibrium conformation.
H ₂ F ₂	Hydrogen fluoride dimer	[H]F. [H]F	Two hydrogen fluoride units joined by a hydrogen bond in a planar equilibrium arrangement.

Ordinary SMILES does not specify these conformations or encode the hydrogen bond between the two components of the hydrogen fluoride dimer.

1. Covalent bond between two equal atoms.

Ethene contains a carbon–carbon bond, hydrazine a nitrogen–nitrogen bond, and hydrogen peroxide an oxygen–oxygen bond. The hydrogen fluoride dimer contains covalent hydrogen–fluorine bonds and a hydrogen bond; it has no covalent fluorine–fluorine or hydrogen–hydrogen bond.

2. Double bond.

Only ethene contains a double bond: its carbon–carbon bond consists of one σ bond and one π bond.

3. Planarity.

Ethene is planar because the carbon atoms are trigonal planar and their parallel p orbitals form the π bond. The hydrogen fluoride dimer is also planar, although it need not be represented as a straight chain. Hydrazine and hydrogen peroxide have nonplanar equilibrium structures.

4. Polarity.

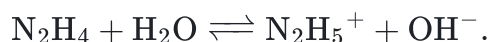
Ethene's symmetry gives a zero permanent molecular dipole moment. The bond dipoles and electron distributions in hydrazine, hydrogen peroxide and the hydrogen fluoride dimer do not cancel, so these three species are polar.

5. Hydrogen bonding within the listed species.

Only the hydrogen fluoride dimer contains a hydrogen bond as part of the specified aggregate: a hydrogen covalently attached to one fluorine interacts with the other fluorine. Individual hydrazine and hydrogen peroxide molecules contain no intramolecular hydrogen bond. Their ability to form hydrogen bonds **between separate molecules** does not warrant a "+" in this row.

6. Basic properties toward water.

Hydrazine accepts a proton from water through a nitrogen lone pair:



Here water is O, the hydrazinium ion is $\text{N}[\text{NH}_3^+]$, and the hydroxide ion is $[\text{OH}^-]$. Formation of hydroxide accounts for the basic solution. Ethene does not appreciably act as a base toward water; hydrogen peroxide and hydrogen fluoride exhibit acidic behavior in water.

b)

For a species with signed charge q , expressed in units of the elementary charge, the total electron count is

$$N_e = \sum_{\text{atoms}} Z - q.$$

Thus a positive charge removes electrons and a negative charge adds electrons.

Replacing a carbon atom by nitrogen increases the nuclear charge by one. Increasing the species' positive charge by one at the same time preserves its electron count. Applying this consistently gives all six pairs in the completed table.

Upper species: name and SMILES	Lower species: name and SMILES	Total-electron check
Methane, CH_4 : C	Ammonium ion, NH_4^+ : $[\text{NH}_4^+]$	$6 + 4 = 7 + 4 - 1 = 10$
Ethane, C_2H_6 : CC	Hydrazine-1,2-diium ion, $\text{N}_2\text{H}_6^{2+}$: $[\text{NH}_3^+][\text{NH}_3^+]$	$2(6) + 6 = 2(7) + 6 - 2 = 18$
Carbonate ion, CO_3^{2-} : $[\text{O}-]\text{C}(=\text{O})[\text{O}-]$	Nitrate ion, NO_3^- : $[\text{O}-][\text{N}^+](=\text{O})[\text{O}-]$	$6 + 3(8) + 2 = 7 + 3(8) + 1 = 32$
Carbon dioxide, CO_2 : $\text{O}=\text{C}=\text{O}$	Nitronium ion, NO_2^+ : $\text{O}=[\text{N}^+]=\text{O}$	$6 + 2(8) = 7 + 2(8) - 1 = 22$
Oxalate ion, $\text{C}_2\text{O}_4^{2-}$: $[\text{O}-]\text{C}(=\text{O})\text{C}(=\text{O})[\text{O}-]$	Dinitrogen tetroxide, N_2O_4 : $[\text{O}-][\text{N}^+](=\text{O})[\text{N}^+](=\text{O})[\text{O}-]$	$2(6) + 4(8) + 2 = 2(7) + 4(8) = 46$
Acetylide dianion (ethynediide), C_2^{2-} : $[\text{C}-]\#[\text{C}-]$	Dinitrogen, N_2 : $\text{N}\#\text{N}$	$2(6) + 2 = 2(7) = 14$

The SMILES show representative Lewis structures; they do not encode resonance delocalization in the oxygen-containing groups.

The corresponding pairs have the same valence-electron counts and analogous bonding arrangements. In particular, carbon dioxide and the nitronium ion are linear, while the acetylide dianion and dinitrogen both have a triple bond and one lone pair on each atom.

Carbon monoxide, CO , SMILES $[\text{C}-]\#[\text{O}^+]$, also has a triple bond, one lone pair on each atom, and

$$N_e = 6 + 8 = 14.$$

It therefore also qualifies for the final blank.

"Identical" here describes the intended electron-count and Lewis-structure correspondence; it does not imply identical orbital energies, bond strengths or other physical properties.

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