

IChO 1968

Theory problems and solutions · Prague, Czechoslovakia · 4 theory problems with complete solutions

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Problem 1: Composition of an irradiated hydrogen-chlorine mixture

A mixture of hydrogen and chlorine kept in a closed flask at a constant temperature was irradiated by scattered light. After a certain time the chlorine content decreased by 20 % compared with that of the starting mixture and the resulting mixture had the composition as follows: 60 volume % of chlorine, 10 volume % of hydrogen, and 30 volume % of hydrogen chloride.

Problems:

1.1 What is the composition of the initial gaseous mixture?

1.2 How chlorine, hydrogen, and hydrogen chloride are produced?

Official English text of the problem.

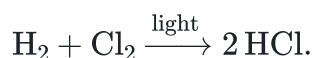
Answers

- **1.1** The initial mixture contained **75 volume % chlorine**, Cl_2 , ClCl , and **25 volume % hydrogen**, H_2 , $[\text{H}][\text{H}]$.
- **1.2** Representative preparations are:
 - **Chlorine**: oxidation of concentrated hydrochloric acid with manganese(IV) oxide; industrially, electrolysis of brine.
 - **Hydrogen**: reaction of zinc with dilute hydrochloric acid; industrially, steam reforming followed by the water-gas shift reaction, or as a coproduct of brine electrolysis.
 - **Hydrogen chloride**, HCl , $[\text{H}]\text{Cl}$: reaction of sodium chloride with concentrated sulfuric acid; industrially, direct combination of hydrogen and chlorine.

Solution

1.1 Initial composition

The light-induced reaction is



For gases at the same temperature and pressure, volume fractions equal mole fractions. The reaction consumes two moles of gaseous reactants for every two moles of gaseous product formed, so the total amount of gas remains unchanged.

Take a basis of **100 mol of the final mixture**:

$$n(\text{Cl}_2) = 60 \text{ mol}, \quad n(\text{H}_2) = 10 \text{ mol}, \quad n(\text{HCl}) = 30 \text{ mol}.$$

The starting mixture contained only hydrogen and chlorine. Formation of 30 mol of hydrogen chloride therefore consumed

$$n_{\text{consumed}}(\text{H}_2) = n_{\text{consumed}}(\text{Cl}_2) = \frac{30}{2} = 15 \text{ mol}.$$

The material balance is:

Gas	Initial amount	Change	Final amount
Cl ₂	75 mol	−15 mol	60 mol
H ₂	25 mol	−15 mol	10 mol
HCl	0 mol	+30 mol	30 mol
Total	100 mol	0 mol	100 mol

Thus,

Initial mixture: 75 volume % Cl₂ and 25 volume % H₂.

The relative decrease in chlorine is

$$\frac{75 - 60}{75} \times 100\% = 20\%,$$

which agrees with the stated decrease.

1.2 Preparation of the gases

The question does not specify a production scale, so representative laboratory and industrial methods are given.

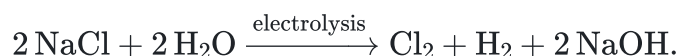
Chlorine

In the laboratory, warming manganese(IV) oxide with concentrated hydrochloric acid produces chlorine:



Manganese is reduced from oxidation state +4 to +2, while chlorine is oxidized from −1 to 0.

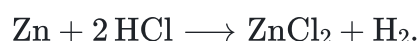
Industrially, concentrated aqueous sodium chloride—brine—is electrolysed:



Chlorine forms at the anode and hydrogen at the cathode. The electrode products are kept separate to permit collection of the gases and prevent their reaction with each other or with the sodium hydroxide solution.

Hydrogen

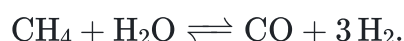
In the laboratory, zinc reacts with dilute hydrochloric acid:



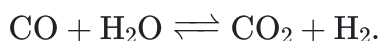
Zinc is oxidized from 0 to +2, and hydrogen is reduced from +1 to 0.

Hydrogen is also obtained industrially as the cathodic product of brine electrolysis, as shown above.

Another major route is the catalytic reaction of methane with steam at high temperature:



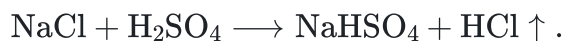
The carbon monoxide is then reacted with further steam in the water-gas shift reaction:



After removal of carbon dioxide and other impurities, hydrogen is obtained.

Hydrogen chloride

In the laboratory, gentle heating of sodium chloride with concentrated sulfuric acid gives hydrogen chloride gas:

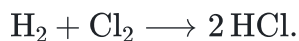


With stronger heating and sufficient sodium chloride, the overall reaction is



The low volatility of sulfuric acid allows volatile hydrogen chloride to be expelled from the mixture.

Industrially, hydrogen chloride can be produced by controlled direct combination of hydrogen and chlorine:



Absorbing the resulting hydrogen chloride gas in water produces hydrochloric acid.

Names and SMILES for the additional substances used above

For salts and extended solids, the dot-separated representations below give formal ionic formula-unit compositions; they do not describe a discrete molecule, a crystal lattice, or solvation.

Formula	Name	SMILES
H ₂ O	Water	O
MnO ₂	Manganese(IV) oxide	[Mn+4].[O-2].[O-2]
MnCl ₂	Manganese(II) chloride	[Mn+2].[Cl-].[Cl-]
NaCl	Sodium chloride	[Na+].[Cl-]
NaOH	Sodium hydroxide	[Na+].[OH-]
ZnCl ₂	Zinc chloride	[Zn+2].[Cl-].[Cl-]
CH ₄	Methane	C
CO	Carbon monoxide	[C-]#[O+]
CO ₂	Carbon dioxide	O=C=O
H ₂ SO ₄	Sulfuric acid	OS(=O)(=O)O
NaHSO ₄	Sodium hydrogen sulfate	[Na+].OS(=O)(=O)[O-]
Na ₂ SO ₄	Sodium sulfate	[Na+].[Na+].[O-]S(=O)(=O)[O-]

Zinc, Zn, is a metallic solid; [zn] represents an individual zinc atom, not its metallic lattice.

The solution was checked against the official solution.

Problem 2: Equations of three redox reactions

Write down equations for the following reactions:

2.1 Oxidation of chromium(III) chloride with bromine in alkaline solution (KOH).

2.2 Oxidation of potassium nitrite with potassium permanganate in acid solution (H₂SO₄).

2.3 Action of chlorine on lime water (Ca(OH)₂) in a cold reaction mixture.

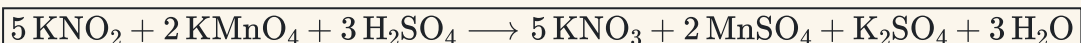
Official English text of the problem.

Answers

• **2.1**



• **2.2**



• **2.3**



Solution

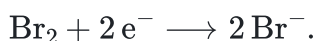
2.1

Bromine oxidizes chromium from oxidation state +3 to +6. In alkaline solution, the resulting chromium(VI) species is **chromate**, CrO₄²⁻. Bromine is reduced from oxidation state 0 to -1, forming **bromide**, Br⁻.

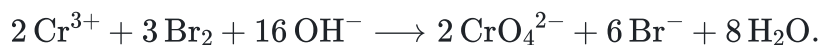
The half-reactions in alkaline solution are



and



Multiplying the first by 2 and the second by 3 balances the transfer of six electrons:



Restoring the potassium and chloride spectator ions gives the molecular equation in **2.1**. The salt products are potassium chromate, potassium bromide, and potassium chloride.

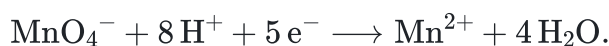
2.2

Nitrogen is oxidized from +3 in **nitrite**, NO₂⁻, to +5 in **nitrate**, NO₃⁻, losing two electrons per nitrogen atom. Manganese is reduced from +7 in **permanganate**, MnO₄⁻, to +2 in acidic solution, gaining five electrons per manganese atom.

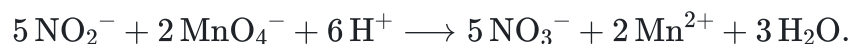
The half-reactions are



and



Multiplying the first by 5 and the second by 2, then cancelling electrons, water, and hydrogen ions, gives



The six hydrogen ions require three formula units of sulfuric acid. Restoring potassium and sulfate gives the equation in **2.2**, with potassium nitrate, manganese(II) sulfate, and potassium sulfate as the salt products.

2.3

In a cold alkaline mixture, chlorine undergoes **disproportionation**:

- One chlorine atom is reduced from 0 to -1 , forming chloride.
- The other is oxidized from 0 to $+1$, forming **hypochlorite**, ClO^- .

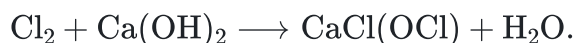
Thus chloride and hypochlorite form in equal amounts. Balancing oxygen and hydrogen with hydroxide and water gives



Calcium remains in oxidation state $+2$. Using calcium hydroxide as the source of hydroxide gives calcium chloride and calcium hypochlorite:



The same stoichiometry can be written using the formal mixed-salt shorthand



Here calcium chloride hypochlorite, $\text{CaCl}(\text{OCl})$, $[\text{Ca}+2] \cdot [\text{Cl}-] \cdot [\text{O}-]\text{Cl}$, records the calcium, chloride, and hypochlorite composition of the aqueous products.

Names and SMILES

The salts in these equations consist of ions; their constituent-ion SMILES are given below, with their proportions specified by the chemical formulas.

Molecule or ion	SMILES
Bromine, Br_2	<chem>BrBr</chem>
Chlorine, Cl_2	<chem>ClCl</chem>
Water, H_2O	<chem>O</chem>
Sulfuric acid, H_2SO_4	<chem>OS(=O)(=O)O</chem>
Hydrogen ion, H^+	<chem>[H+]</chem>
Hydroxide ion, OH^-	<chem>[OH-]</chem>
Potassium ion, K^+	<chem>[K+]</chem>
Calcium ion, Ca^{2+}	<chem>[Ca+2]</chem>
Chromium(III) ion, Cr^{3+}	<chem>[Cr+3]</chem>
Manganese(II) ion, Mn^{2+}	<chem>[Mn+2]</chem>
Chloride ion, Cl^-	<chem>[Cl-]</chem>
Bromide ion, Br^-	<chem>[Br-]</chem>
Chromate ion, CrO_4^{2-}	<chem>[O-][Cr](=O)(=O)[O-]</chem>

Molecule or ion	SMILES
Nitrite ion, NO_2^-	<chem>[O-]N=O</chem>
Nitrate ion, NO_3^-	<chem>[O-][N+](=O)[O-]</chem>
Permanganate ion, MnO_4^-	<chem>[O-][Mn](=O)(=O)=O</chem>
Sulfate ion, SO_4^{2-}	<chem>[O-]S(=O)(=O)[O-]</chem>
Hypochlorite ion, ClO^-	<chem>[O-]Cl</chem>

These SMILES do not specify solvation or ionic crystal structures. Chromate, permanganate, and sulfate have tetrahedral oxygen arrangements around their central atoms; nitrate is trigonal planar, and nitrite is bent. The oxoanion SMILES show representative resonance forms rather than a unique localization of bonds and charge.

The solution was checked against the official solution.

Problem 3: Combustion of blast-furnace gas

The gas escaping from a blast furnace has the following composition:

12.0 volume % of CO_2	28.0 volume % of CO
3.0 volume % of H_2	0.6 volume % of CH_4
0.2 volume % of C_2H_4	56.2 volume % of N_2

Problems:

3.1 Calculate the theoretical consumption of air (in m^3) which is necessary for a total combustion of 200 m^3 of the above gas if both the gas and air are measured at the same temperature. (Oxygen content in the air is about 20 % by volume).

3.2 Determine the composition of combustion products if the gas is burned in a 20 % excess of air.

Official English text of the problem.

Answers

- 3.1:** The theoretical air requirement is 173 m^3 .
- 3.2:** With 20% excess air, the product compositions are approximately:

Product: name, formula, SMILES	Wet basis (volume %)	Dry basis (volume %)
Carbon dioxide, CO_2 , <chem>O=C=O</chem>	21.8	22.3
Water, H_2O , <chem>O</chem>	2.4	Removed
Oxygen, O_2 , <chem>O=O</chem>	1.8	1.9
Nitrogen, N_2 , <chem>N#N</chem>	74.0	75.8

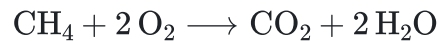
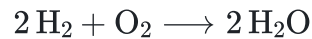
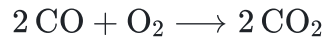
The wet composition assumes all water remains as vapour; the dry composition excludes water.

Solution

3.1

At the same temperature and pressure, ideal-gas volumes are proportional to amounts in moles. Thus, balanced equations also give the reacting gas-volume ratios.

The combustible constituents are carbon monoxide (CO , $[\text{C-}][\text{O+}]$), hydrogen (H_2 , $[\text{H}][\text{H}]$), methane (CH_4 , C), and ethene (C_2H_4 , $\text{C}=\text{C}$). Their complete combustion reactions are:



The carbon dioxide already present requires no oxygen, and nitrogen is treated as inert.

For 200 m^3 of blast-furnace gas:

Combustible gas	Initial volume (m^3)	Oxygen required per unit gas volume	Required oxygen (m^3)
CO	$200(0.280) = 56.0$	$1/2$	28.0
H_2	$200(0.030) = 6.0$	$1/2$	3.0
CH_4	$200(0.006) = 1.2$	2	2.4
C_2H_4	$200(0.002) = 0.4$	3	1.2

Hence,

$$V_{\text{O}_2, \text{required}} = 28.0 + 3.0 + 2.4 + 1.2 = 34.6 \text{ m}^3.$$

Since air contains 20% oxygen by volume,

$$V_{\text{air, theoretical}} = \frac{34.6}{0.20} = 173 \text{ m}^3.$$

3.2

A 20% excess means supplying 1.20 times the theoretical air requirement:

$$V_{\text{air, supplied}} = 1.20(173) = 207.6 \text{ m}^3.$$

Taking the remaining 80% of air as nitrogen, this supplies

$$V_{\text{O}_2, \text{supplied}} = 0.20(207.6) = 41.52 \text{ m}^3,$$

$$V_{\text{N}_2, \text{air}} = 0.80(207.6) = 166.08 \text{ m}^3.$$

All following product volumes are expressed at the same reference temperature and pressure, with water treated as vapour.

Carbon dioxide consists of the original carbon dioxide plus that formed from carbon monoxide, methane, and ethene:

$$\begin{aligned} V_{\text{CO}_2} &= 200(0.120) + 56.0 + 1.2 + 2(0.4) \\ &= \boxed{82.0 \text{ m}^3}. \end{aligned}$$

Water is formed from hydrogen, methane, and ethene:

$$V_{\text{H}_2\text{O}} = 6.0 + 2(1.2) + 2(0.4) = \boxed{9.2 \text{ m}^3}.$$

The unconsumed oxygen is

$$V_{\text{O}_2} = 41.52 - 34.6 = \boxed{6.92 \text{ m}^3}.$$

Nitrogen comes from both the fuel gas and the supplied air:

$$V_{\text{N}_2} = 200(0.562) + 166.08 = \boxed{278.48 \text{ m}^3}.$$

Thus, the total wet product volume is

$$V_{\text{wet}} = 82.0 + 9.2 + 6.92 + 278.48 = 376.6 \text{ m}^3.$$

Each wet volume percentage is calculated from

$$\text{Volume percentage of species } i = \frac{V_i}{376.6 \text{ m}^3} \times 100\%.$$

For example,

$$\text{Wet CO}_2 \text{ percentage} = \frac{82.0}{376.6} \times 100\% \approx 21.8\%.$$

For the dry composition, exclude the water:

$$V_{\text{dry}} = 376.6 - 9.2 = 367.4 \text{ m}^3.$$

Dividing the volumes of carbon dioxide, oxygen, and nitrogen by 367.4 m^3 gives the dry percentages reported above.

The solution was checked against the official solution.

Problem 4: Identification of an organic acid from titration and vapour density

A volume of 31.7 cm^3 of a 0.1-normal NaOH is required for the neutralization of 0.19 g of an organic acid whose vapour is thirty times as dense as gaseous hydrogen.

Problem:

4.1 Give the name and structural formula of the acid.

(The acid concerned is a common organic acid.)

Official English text of the problem.

Answers

- 4.1 Acetic acid (ethanoic acid)**, structural formula $\text{CH}_3\text{--C}(=\text{O})\text{--OH}$; SMILES: CC(=O)O.

Solution

4.1

At the same temperature and pressure, gas densities are proportional to molar masses. Gaseous hydrogen, H_2 , SMILES [H][H], has molar mass approximately 2 g mol^{-1} . Therefore, the acid has molar mass

$$M_{\text{acid}} = 30M_{\text{H}_2} \approx 30 \times 2 = 60 \text{ g mol}^{-1}.$$

The amount of base used, expressed in equivalents, is

$$n_{\text{eq}} = NV = (0.1 \text{ eq L}^{-1}) (31.7 \times 10^{-3} \text{ L}) = 3.17 \times 10^{-3} \text{ eq}.$$

Thus, the acid's equivalent mass is

$$E = \frac{0.19 \text{ g}}{3.17 \times 10^{-3} \text{ eq}} \approx 59.9 \text{ g eq}^{-1}.$$

The number of neutralizable protons per molecule is consequently

$$z = \frac{M_{\text{acid}}}{E} \approx \frac{60}{59.9} \approx 1.$$

The small discrepancy from an exact integer reflects rounding of the supplied data. The acid is therefore **monoprotic**.

The common organic acid satisfying these conditions is **acetic acid (ethanoic acid)**, SMILES CC(=O)O. Its molecular formula is $\text{C}_2\text{H}_4\text{O}_2$, giving

$$M = (2 \times 12 + 4 \times 1 + 2 \times 16) \text{ g mol}^{-1} = 60 \text{ g mol}^{-1}.$$

Its structural formula is $\text{CH}_3\text{--C(=O)--OH}$: a methyl group bonded to a carboxyl group. The carboxyl proton is neutralized according to



Here sodium hydroxide is [Na+].[OH-], sodium acetate is CC(=O)[O-].[Na+], and water is O. This reaction confirms the required 1 : 1 acid-to-base stoichiometry.

The solution was checked against the official solution.