

IChO 1969

Theory problems and solutions · Katowice, Poland · 4 theory problems with complete solutions

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Problem 1: Electrolysis of a potassium sulphate solution

An amount of 20 g of potassium sulphate was dissolved in 150 cm³ of water. The solution was then electrolysed. After electrolysis, the content of potassium sulphate in the solution was 15 % by mass.

Problem:

What volumes of hydrogen and oxygen were obtained at a temperature of 20 °C and a pressure of 101 325 Pa?

Official English text of the problem.

Answers

- **Problem 1:** Hydrogen, H₂ ([H][H]): 49.0 dm³; oxygen, O₂ (O=O): 24.5 dm³.

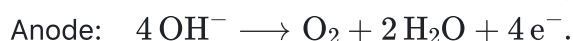
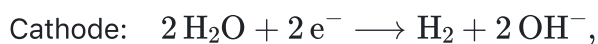
Solution

Problem 1

Assume ordinary electrolysis with inert electrodes, a water density of 1.00 g cm⁻³, negligible evaporation, and ideal gas behaviour.

Potassium sulphate, K₂SO₄ ([K+].[K+].[O-]S(=O)(=O)[O-]), acts as the electrolyte and remains in the solution. Water, H₂O (o), is decomposed into hydrogen and oxygen.

The electrode reactions, written using hydroxide ions, OH⁻ ([OH-]), are



Doubling the cathode reaction and adding gives



Thus, the solution loses mass as the gaseous products escape, while its potassium sulphate content remains 20 g.

The initial mass of solution is

$$m_{\text{initial}} = 20 \text{ g} + (150 \text{ cm}^3)(1.00 \text{ g cm}^{-3}) = 170 \text{ g}.$$

Since the final solution contains 15% potassium sulphate by mass,

$$0.15 = \frac{20 \text{ g}}{m_{\text{final}}}, \quad m_{\text{final}} = \frac{20}{0.15} = 133.333 \dots \text{ g}.$$

The mass of water decomposed is therefore

$$m(\text{H}_2\text{O}) = 170 - 133.333 \dots = 36.666 \dots \text{ g}.$$

Using $M(\text{H}_2\text{O}) = 18.0 \text{ g mol}^{-1}$,

$$n(\text{H}_2\text{O}) = \frac{36.666 \dots \text{ g}}{18.0 \text{ g mol}^{-1}} = 2.037 \dots \text{ mol}.$$

The overall reaction gives

$$n(\text{H}_2) = 2.037 \dots \text{ mol}, \quad n(\text{O}_2) = 1.0185 \dots \text{ mol}.$$

At $T = 293.15 \text{ K}$ and $p = 101\,325 \text{ Pa}$, apply $V = nRT/p$, with $R = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$:

$$V(\text{H}_2) = \frac{(2.037 \dots)(8.314)(293.15)}{101\,325} \text{ m}^3 = \boxed{49.0 \text{ dm}^3}.$$

At the same temperature and pressure, oxygen occupies half the hydrogen volume:

$$V(\text{O}_2) = \frac{1}{2} V(\text{H}_2) = \boxed{24.5 \text{ dm}^3}.$$

The solution was checked against the official solution.

Problem 2: Two potassium-nitrogen-oxygen compounds

A compound **A** contains 38.67 % of potassium, 13.85 % of nitrogen, and 47.48 % of oxygen. On heating, it is converted to a compound **B** containing 45.85 % of potassium, 16.47 % of nitrogen, and 37.66 % of oxygen.

Problem:

2.1 What are the stoichiometric formulas of the compounds?

2.2 Write the corresponding chemical equation.

Official English text of the problem.

Answers

- 2.1** **A** is potassium nitrate, KNO_3 , SMILES $[\text{K}^+] \cdot [\text{O}^-] [\text{N}^+] (= \text{O}) [\text{O}^-]$. **B** is potassium nitrite, KNO_2 , SMILES $[\text{K}^+] \cdot [\text{O}^-] \text{N}=\text{O}$.
- 2.2**



The gas evolved is dioxygen, SMILES $\text{O}=\text{O}$.

The salt SMILES specify the constituent ions in one formula unit; they do not describe the crystal lattice.

Solution

2.1

Take a 100.00 g sample of each compound. The elemental masses in grams then equal the given percentage values. Using atomic molar masses

$$M(\text{K}) = 39.10, \quad M(\text{N}) = 14.01, \quad M(\text{O}) = 16.00 \text{ g mol}^{-1},$$

calculate each amount from $n = m/M$. For example, for potassium in **A**,

$$n(\text{K}) = \frac{38.67 \text{ g}}{39.10 \text{ g mol}^{-1}} = 0.9890 \text{ mol}.$$

Compound	$n(\text{K}), \text{ mol}$	$n(\text{N}), \text{ mol}$	$n(\text{O}), \text{ mol}$
A	0.9890	0.9886	2.968
B	1.173	1.176	2.354

Dividing by the nitrogen amount in each compound gives the atomic ratios:

$$\mathbf{A} : \quad \text{K} : \text{N} : \text{O} \approx 1.000 : 1.000 : 3.002 \approx 1 : 1 : 3,$$

$$\mathbf{B} : \quad \text{K} : \text{N} : \text{O} \approx 0.9975 : 1.000 : 2.002 \approx 1 : 1 : 2.$$

Therefore the stoichiometric formulas are



2.2

On heating, potassium nitrate decomposes into potassium nitrite and oxygen. The formula change retains potassium and nitrogen while removing one oxygen atom per formula unit. Consequently, two formula units release one molecule of dioxygen:



Both sides contain two potassium atoms, two nitrogen atoms, and six oxygen atoms.

The solution was checked against the official solution.

Problem 3: Combustion analysis of a gaseous hydrocarbon

A 10 cm³ sample of an unknown gaseous hydrocarbon was mixed with 70 cm³ of oxygen and the mixture was set on fire by means of an electric spark. When the reaction was over and water vapours were liquefied, the final volume of gases decreased to 65 cm³. This mixture then reacted with a potassium hydroxide solution and the volume of gases decreased to 45 cm³.

Problem:

What is the molecular formula of the unknown hydrocarbon if volumes of gases were measured at standard temperature and pressure (STP) conditions?

Answers

- 3. $\boxed{\text{C}_2\text{H}_2}$: **ethyne (acetylene)**, SMILES C#C.

Solution

3. Let the hydrocarbon have molecular formula C_xH_y . Its complete combustion follows



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

After water, SMILES O, has condensed, the remaining gases are carbon dioxide, SMILES O=C=O, and excess oxygen, SMILES O=O.

Potassium hydroxide, SMILES [K+] . [OH-], absorbs carbon dioxide. With excess alkali, this reaction is



forming potassium carbonate, SMILES [K+] . [K+] . [O-]C(=O)[O-].

Thus the volume of carbon dioxide produced is

$$V_{\text{CO}_2} = (65 - 45) \text{ cm}^3 = 20 \text{ cm}^3.$$

Each mole of hydrocarbon produces x moles of carbon dioxide, so

$$x = \frac{20 \text{ cm}^3}{10 \text{ cm}^3} = 2.$$

The gas remaining after absorption is unused oxygen. Therefore,

$$V_{\text{O}_2, \text{ consumed}} = (70 - 45) \text{ cm}^3 = 25 \text{ cm}^3.$$

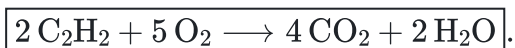
The combustion equation then gives

$$x + \frac{y}{4} = \frac{25 \text{ cm}^3}{10 \text{ cm}^3} = 2.5.$$

Substituting $x = 2$,

$$2 + \frac{y}{4} = 2.5 \implies y = 2.$$

Hence the hydrocarbon is **ethyne (acetylene)**, C_2H_2 , SMILES C#C, whose balanced combustion equation is



As a check, 10 cm^3 of ethyne consumes 25 cm^3 of oxygen and produces 20 cm^3 of carbon dioxide. After condensation, the gas volume is $45 + 20 = 65 \text{ cm}^3$; carbon dioxide absorption leaves 45 cm^3 , matching both observations.

The solution was checked against the official solution.

Problem 4: Products obtainable from calcium carbide and water

Calcium carbide and water are the basic raw materials in the production of:

- a) ethanol
- b) acetic acid
- c) ethylene and polyethylene
- d) vinyl chloride
- e) benzene

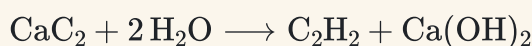
Problem:

Give basic chemical equations for each reaction by which the above mentioned compounds can be obtained.

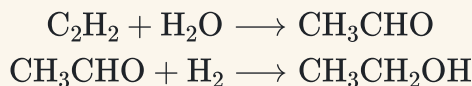
Official English text of the problem.

Answers

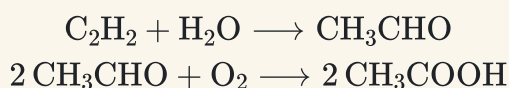
All routes start with the formation of acetylene (ethyne), $C\equiv C$:



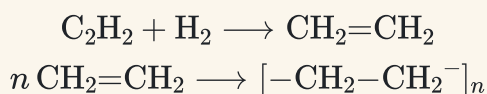
- **a) Ethanol**, CCO : hydrate acetylene to ethanal, then hydrogenate.



- **b) Acetic acid**, $CC(=O)O$: hydrate acetylene to ethanal, then oxidize.

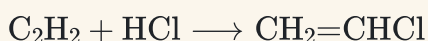


- **c) Ethylene (ethene)**, $C=C$, and **polyethylene**, repeat-unit SMILES $[*]CC[*]$: partially hydrogenate acetylene, then polymerize.

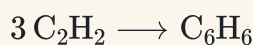


The stars in the repeat-unit SMILES mark connections to the continuing chain; a complete molecular SMILES would require a specified chain length and end groups.

- **d) Vinyl chloride (chloroethene)**, $C=CCl$: add hydrogen chloride to acetylene.



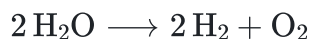
- **e) Benzene**, $c1ccccc1$: cyclotrimerize acetylene.



Solution

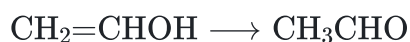
The common starting reaction is the hydrolysis of calcium carbide. Water protonates its acetylide component, releasing acetylene and leaving calcium hydroxide. The substances are calcium carbide, $[\text{Ca}+2] \cdot [\text{C}-]\#[\text{C}-]$; water, O ; and calcium hydroxide, $[\text{Ca}+2] \cdot [\text{OH}-] \cdot [\text{OH}-]$. The disconnected salt SMILES represent ionic formula units, not discrete molecules.

Hydrogen, $[\text{H}][\text{H}]$, and oxygen, $\text{O}=\text{O}$, are auxiliary reagents in the routes below. They can also be obtained from water by electrolysis:



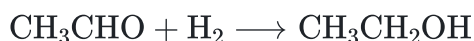
a) Ethanol

Hydration of acetylene in acidic aqueous solution, catalysed by mercury(II) ions, $[\text{Hg}+2]$, gives ethanal (acetaldehyde), $\text{CC}=\text{O}$. The initially formed enol is vinyl alcohol (ethenol), $\text{C}=\text{CO}$, which rearranges by keto–enol tautomerism:



Thus the net hydration equation is $\text{C}_2\text{H}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CHO}$.

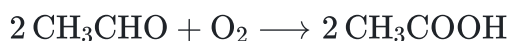
Catalytic hydrogenation of ethanal, for example over nickel, reduces its carbonyl group to a primary alcohol:



The two-carbon skeleton is retained, giving ethanol.

b) Acetic acid

First prepare ethanal by the same hydration reaction as in (a). Oxidation converts its aldehyde group into a carboxyl group:



Each ethanal molecule gains one oxygen atom, so one molecule of oxygen oxidizes two molecules of ethanal.

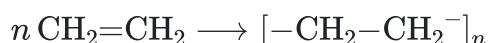
c) Ethylene and polyethylene

Selective catalytic hydrogenation adds one molecule of hydrogen across part of acetylene's triple bond:



The catalyst and reaction conditions must favour stopping at ethylene.

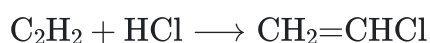
Ethylene then undergoes addition polymerization, for example using high temperature and pressure with radical initiation:



The double bonds become single bonds as the monomers join into a chain. Every monomer contributes one $-\text{CH}_2-\text{CH}_2-$ repeat unit, without elimination of a small molecule.

d) Vinyl chloride

Hydrogen chloride, Cl , adds across acetylene's triple bond. A conventional catalyst is mercury(II) chloride, $\text{Cl}[\text{Hg}]\text{Cl}$:



Addition of one equivalent gives a double bond bearing one chlorine substituent: vinyl chloride. Hydrogen chloride supplies the chlorine, which is absent from the two basic raw materials.

e) Benzene

On heating over a suitable catalyst, such as activated carbon, three acetylene molecules undergo cyclotrimerization:



Their six carbon atoms form the aromatic six-membered ring of benzene. All six hydrogen atoms are retained, and no coproduct is required.

The solution was checked against the official solution.