

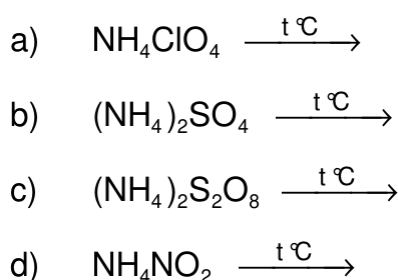
# IChO 1983

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## Problem 1: Short questions A-J in inorganic and general chemistry

A) Describe the thermal decomposition of the following ammonium salts in terms of chemical equations:



B) Indicate the right answer:

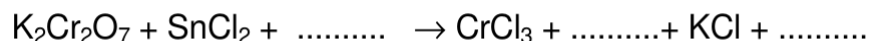
a) Can the molar mass be determined by measuring the density of a gaseous compound at a given temperature and pressure?

1. Yes, under any conditions.
2. Yes, if the gaseous compound does not dissociate and associate.
3. Yes, if the gaseous compound does not dissociate.
4. Yes, if the gaseous compound does not associate.

b) Is a liquid boiling at a constant temperature (at a given pressure) a pure substance?

1. Yes, if the liquid is not azeotropic.
2. Yes, if the liquid is azeotropic.

C) Complete and balance the following equation: (in  $\text{H}_2\text{O}$ )



D) The solubility of  $\text{Hg}_2\text{Cl}_2$  in water is  $3.0 \times 10^{-5}$  g/100 ml solution.

a) What is the solubility product?

b) What is the solubility (in  $\text{mol dm}^{-3}$ ) of this substance in a 0.01 M NaCl solution?

c) What is the volume of a 0.01 M NaCl solution which dissolves the same quantity of mercurous chloride as that dissolved in one litre of pure water?

$$A_r(\text{Hg}) = 200.61 \quad A_r(\text{Cl}) = 35.45$$

E) Which of the following groups contains solid compounds at 10 °C?

- a)  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$
- b)  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$
- c)  $\text{SO}_3$ ,  $\text{I}_2$ ,  $\text{NaCl}$
- d)  $\text{Si}$ ,  $\text{S}_8$ ,  $\text{Hg}$

F) Which of the following salts forms an acidic aqueous solution?

- a)  $\text{CH}_3\text{COONa}$
- b)  $\text{NH}_4\text{Cl}$
- c)  $\text{Na}_2\text{HPO}_4$
- d)  $\text{Na}_2\text{CO}_3$
- e)  $\text{NaHCO}_3$

G) Write the electronic formulas for the following compounds so that the nature of the chemical bonds is evident:

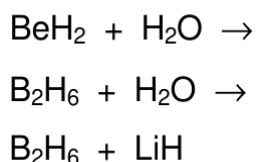
- a)  $\text{NaClO}_3$ , b)  $\text{HClO}_3$ , c)  $\text{SiF}_4$ , d)  $\text{NH}_3$ , e)  $\text{CaF}_2$ , f)  $\text{H}_2\text{O}$

H) Solid perchloric acid is usually written as  $\text{HClO}_4 \cdot \text{H}_2\text{O}$ . Based on experimental data showing four equal bonds, suggest a structure accounting for the experimental result.

I) The compounds of the second row elements with hydrogen are as follows:

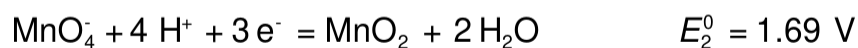
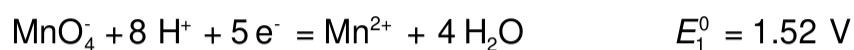
$\text{LiH}$ ,  $\text{BeH}_2$ ,  $\text{B}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$ .

- a) Which compounds are solid at room temperature? Explain.
- b) Which of them are ionic?
- c) Which are polymeric?
- d) Which ones do not react with water under normal conditions?
- e) Give products of the following reactions.

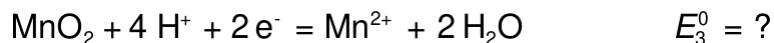


f) Supposing that  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  are acids under some conditions, write their corresponding conjugated bases and arrange them in order of increasing basic strength.

J) The following  $E^0$  values are given for the half-reactions:



Calculate  $E^0$  for the following reaction:

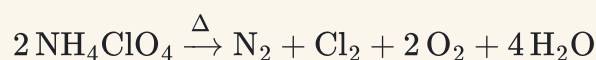


Official English text of the problem.

## Answers

Names and SMILES are supplied with the corresponding explanations in the Solution.

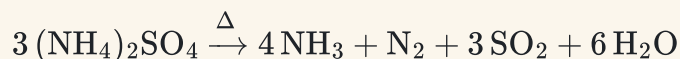
- **A(a)**



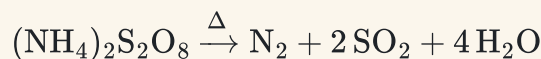
- **A(b)** Initially:



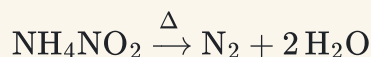
An overall equation for stronger heating is:



- **A(c)**



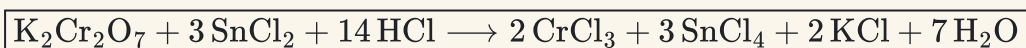
- **A(d)**



- **B(a)** 2, under the usual ideal-gas assumption.

- **B(b)** 1.

- **C)**



- **D(a)**  $K_{\text{sp}} = 1.0 \times 10^{-18}$ , using concentrations expressed in  $\text{mol dm}^{-3}$ .

- **D(b)**  $s = 1.0 \times 10^{-14} \text{ mol dm}^{-3}$ .

- **D(c)**  $V = 6.2 \times 10^7 \text{ dm}^3 = 6.2 \times 10^7 \text{ L}$ .

- **E) c):**  $\text{SO}_3$ ,  $\text{I}_2$ ,  $\text{NaCl}$ .

- **F) b):** ammonium chloride,  $\text{NH}_4\text{Cl}$ .

- **G(a)** Separate  $\text{Na}^+$  and  $\text{ClO}_3^-$  ions; covalent bonds within the trigonal-pyramidal chlorate ion.

- **G(b)**  $\text{H}-\text{O}-\text{Cl}(=\text{O})_2$ , with one lone pair on chlorine; polar covalent bonds.

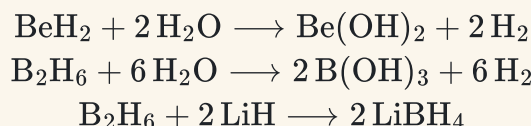
- **G(c)** Tetrahedral  $\text{SiF}_4$ , with four single bonds and three lone pairs on each fluorine.

- **G(d)** Trigonal-pyramidal  $\text{NH}_3$ , with three single bonds and one lone pair on nitrogen.

- **G(e)** Separate  $\text{Ca}^{2+}$  and two  $\text{F}^-$  ions; ionic bonding.

- **G(f)** Bent  $\text{H}_2\text{O}$ , with two single bonds and two lone pairs on oxygen.

- **H)** Hydronium perchlorate,  $[\text{H}_3\text{O}]^+[\text{ClO}_4]^-$ , containing a tetrahedral perchlorate ion with four equivalent chlorine–oxygen bonds.
- **I(a)** LiH and  $\text{BeH}_2$ .
- **I(b)** LiH.
- **I(c)**  $\text{BeH}_2$ .
- **I(d)**  $\text{CH}_4$ ; also  $\text{H}_2\text{O}$  in the trivial sense of adding water to water.
- **I(e)**



- **I(f)** The conjugate bases are  $\text{NH}_2^-$ ,  $\text{OH}^-$ , and  $\text{F}^-$ , respectively. Increasing basic strength:



- **J)**

$$\boxed{E_3^0 = 1.265 \text{ V} \approx 1.27 \text{ V}}$$

## Solution

SMILES below describe molecular connectivity or the constituent ions of a salt. They do not show lone pairs, resonance delocalization, hydrogen bonding, or crystal lattices. Formula-unit and schematic representations of extended or multicentre structures are identified explicitly.

### A) Thermal decomposition

The equations below are conventional overall descriptions. Heating can proceed through intermediate stages, particularly for ammonium sulfate.

**A(a)** Ammonium perchlorate,  $[\text{NH}_4^+] \cdot [\text{O}^-]\text{Cl}(=\text{O})(=\text{O})=\text{O}$ :



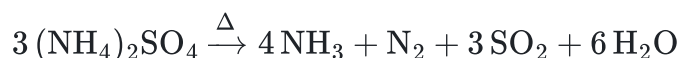
This is internal oxidation–reduction. Nitrogen changes from oxidation state  $-3$  to  $0$ , chlorine from  $+7$  to  $0$ , and some oxygen from  $-2$  to  $0$ . The equation conserves every element and balances the electron transfers.

**A(b)** Ammonium sulfate,  $[\text{NH}_4^+] \cdot [\text{NH}_4^+] \cdot [\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$ , first loses ammonia:



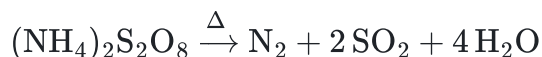
The residual salt is ammonium hydrogen sulfate,  $[\text{NH}_4^+] \cdot \text{OS}(=\text{O})(=\text{O})[\text{O}^-]$ .

On stronger heating, an overall decomposition equation is:



Two of the six nitrogen atoms are oxidized from  $-3$  to  $0$ , releasing six electrons. The three sulfur atoms are reduced from  $+6$  to  $+4$ , accepting six electrons. The remaining nitrogen leaves as ammonia.

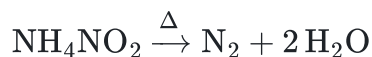
**A(c)** Ammonium peroxodisulfate,  $[\text{NH}_4^+] \cdot [\text{NH}_4^+] \cdot [\text{O}^-]\text{S}(=\text{O})(=\text{O})\text{OOS}(=\text{O})(=\text{O})[\text{O}^-]$ :



The anion contains an oxygen–oxygen peroxide linkage. Its two peroxide oxygen atoms have oxidation state  $-1$ ; its other oxygen atoms have oxidation state  $-2$ .

The two nitrogen atoms release six electrons on oxidation to nitrogen. Reduction of the two sulfur atoms from  $+6$  to  $+4$  consumes four electrons, and reduction of the two peroxide oxygen atoms to  $-2$  consumes the remaining two.

**A(d)** Ammonium nitrite,  $[\text{NH}_4^+] \cdot [\text{O}-]\text{N}=\text{O}$ :



The nitrogen atoms initially have oxidation states  $-3$  and  $+3$ . They combine to form nitrogen in oxidation state  $0$ .

The product identities used in A are:

| Species              | Name           | SMILES             |
|----------------------|----------------|--------------------|
| $\text{N}_2$         | Nitrogen       | <chem>N#N</chem>   |
| $\text{Cl}_2$        | Chlorine       | <chem>ClCl</chem>  |
| $\text{O}_2$         | Oxygen         | <chem>O=O</chem>   |
| $\text{H}_2\text{O}$ | Water          | <chem>O</chem>     |
| $\text{NH}_3$        | Ammonia        | <chem>N</chem>     |
| $\text{SO}_2$        | Sulfur dioxide | <chem>O=S=O</chem> |

## B) Physical properties and composition

**B(a)** For an ideal gas,

$$pV = nRT = \frac{m}{M}RT.$$

Since  $\rho = m/V$ ,

$$M = \frac{\rho RT}{p}.$$

Association or dissociation changes the number of gas particles corresponding to a given mass. The density then gives an apparent average molar mass of the equilibrium mixture, rather than directly giving the molar mass of the original compound. Thus **option 2** is intended.

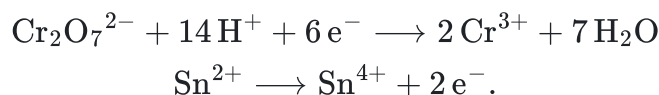
If nonideality matters, a known compressibility factor  $Z$  is also required:

$$M = \frac{\rho ZRT}{p}.$$

**B(b)** A pure liquid boils at a fixed temperature at fixed pressure. However, an azeotropic mixture also boils at a constant temperature because its equilibrium vapour has the same composition as the liquid. Consequently, constant boiling temperature indicates purity only after excluding an azeotrope: **option 1**.

## C) Dichromate oxidation of tin(II)

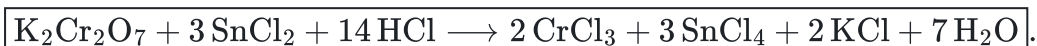
The reduction and oxidation half-reactions are:



Multiplying the second equation by three and adding gives:



Hydrochloric acid supplies the required acidity and chloride. Restoring the potassium and chloride ions gives:



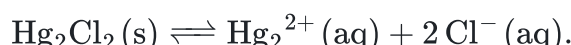
There are 20 chlorine atoms on each side:  $6 + 14 = 6 + 12 + 2$ .

| Substance                         | Name                                          | SMILES                                      |
|-----------------------------------|-----------------------------------------------|---------------------------------------------|
| $\text{K}_2\text{Cr}_2\text{O}_7$ | Potassium dichromate                          | [K+].[K+].[O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-] |
| $\text{SnCl}_2$                   | Tin(II) chloride                              | [Sn+2].[Cl-].[Cl-]                          |
| $\text{HCl}$                      | Hydrogen chloride; hydrochloric acid in water | Cl                                          |
| $\text{CrCl}_3$                   | Chromium(III) chloride                        | [Cr+3].[Cl-].[Cl-].[Cl-]                    |
| $\text{SnCl}_4$                   | Tin(IV) chloride                              | Cl[Sn](Cl)(Cl)Cl                            |
| $\text{KCl}$                      | Potassium chloride                            | [K+].[Cl-]                                  |

The half-reaction species are dichromate ion  $[\text{O-}][\text{Cr}](=\text{O})(=\text{O})\text{O}[\text{Cr}](=\text{O})(=\text{O})[\text{O-}]$ , chromium(III) ion  $[\text{Cr}+3]$ , tin(II) ion  $[\text{Sn}+2]$ , tin(IV) ion  $[\text{Sn}+4]$ , and hydrogen ion  $[\text{H}+]$ . The aqueous hydrogen ion is solvated; the bare-proton notation is conventional shorthand.

## D) Solubility of mercury(I) chloride

Mercury(I) chloride, or calomel, has the structural-unit SMILES  $\text{Cl}[\text{Hg}][\text{Hg}]\text{Cl}$ . Its dissolution equilibrium is:



The mercury(I) cation is the bonded dimer  $\text{Hg}_2^{2+}$ ,  $[\text{Hg}+][\text{Hg}+]$ ; chloride ion is  $[\text{Cl-}]$ .

We use the concentration approximation to activities and the dissolution equilibrium specified by the problem.

**D(a)** The molar mass is

$$M(\text{Hg}_2\text{Cl}_2) = 2(200.61) + 2(35.45) = 472.12 \text{ g mol}^{-1}.$$

The mass solubility is

$$\frac{3.0 \times 10^{-5} \text{ g}}{0.100 \text{ dm}^3} = 3.0 \times 10^{-4} \text{ g dm}^{-3}.$$

Thus the molar solubility in pure water is

$$s_0 = \frac{3.0 \times 10^{-4} \text{ g dm}^{-3}}{472.12 \text{ g mol}^{-1}} = 6.3543 \times 10^{-7} \text{ mol dm}^{-3}.$$

Because

$$[\text{Hg}_2^{2+}] = s_0, \quad [\text{Cl}^-] = 2s_0,$$

the concentration-form solubility product is

$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = s_0(2s_0)^2 = 4s_0^3.$$

Therefore,

$$K_{\text{sp}} = 1.0263 \times 10^{-18} \text{ mol}^3 \text{ dm}^{-9} \approx \boxed{1.0 \times 10^{-18} \text{ mol}^3 \text{ dm}^{-9}}.$$

The corresponding thermodynamic equilibrium constant is dimensionless when activities are referenced to the standard concentration.

**D(b)** Sodium chloride,  $[\text{Na}^+] \cdot [\text{Cl}^-]$ , supplies the common chloride ion. If the new solubility is  $s$ ,

$$K_{\text{sp}} = s(0.010 + 2s)^2.$$

Since  $2s \ll 0.010 \text{ mol dm}^{-3}$ ,

$$s \approx \frac{1.0263 \times 10^{-18}}{(0.010)^2} = 1.0263 \times 10^{-14} \text{ mol dm}^{-3}.$$

Hence

$$\boxed{s = 1.0 \times 10^{-14} \text{ mol dm}^{-3}}.$$

The added chloride from dissolution is only about  $2 \times 10^{-12}$  of the initial chloride concentration, validating the approximation.

**D(c)** One litre of pure water dissolves

$$n = s_0(1.000 \text{ dm}^3) = 6.3543 \times 10^{-7} \text{ mol}.$$

The volume of sodium chloride solution required to dissolve this amount is

$$V = \frac{n}{s} = \frac{6.3543 \times 10^{-7} \text{ mol}}{1.0263 \times 10^{-14} \text{ mol dm}^{-3}} = 6.1916 \times 10^7 \text{ dm}^3.$$

Thus

$$\boxed{V = 6.2 \times 10^7 \text{ L}}.$$

## E) Physical states at 10 °C

At ordinary atmospheric pressure:

| Group | Substances, names and SMILES                                                              | States at 10 °C      |
|-------|-------------------------------------------------------------------------------------------|----------------------|
| a     | Water O; ammonia N; methane C                                                             | Liquid; gas; gas     |
| b     | Fluorine FF; chlorine ClCl; bromine BrBr                                                  | Gas; gas; liquid     |
| c     | Sulfur trioxide O=S(=O)=O; iodine II; sodium chloride $[\text{Na}^+] \cdot [\text{Cl}^-]$ | All solid            |
| d     | Silicon [Si]; cyclooctasulfur S1SSSSSSS1; mercury [Hg]                                    | Solid; solid; liquid |

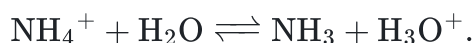
Therefore **group c** is correct.

The sulfur trioxide SMILES describes the monomeric unit; its solid forms can contain associated or polymeric structures. The silicon and mercury symbols likewise do not encode their extended condensed phases.

## F) Acidic salt solution

The answer is **ammonium chloride**,  $[\text{NH}_4^+] \cdot [\text{Cl}^-]$ .

Ammonium ion,  $[\text{NH}_4^+]$ , is the conjugate acid of ammonia and transfers a proton to water:



Production of hydronium ion,  $[\text{H}_3\text{O}^+]$ , makes the solution acidic. Chloride contributes negligible basicity in water.

The other choices give basic solutions:

| Salt                      | Name and SMILES                                                        | Reason                                                                |
|---------------------------|------------------------------------------------------------------------|-----------------------------------------------------------------------|
| $\text{CH}_3\text{COONa}$ | Sodium acetate, <chem>CC(=O)[O-].[Na+]</chem>                          | Acetate accepts a proton from water.                                  |
| $\text{Na}_2\text{HPO}_4$ | Disodium hydrogen phosphate, <chem>[Na+].[Na+].OP(=O)([O-])[O-]</chem> | Hydrogen phosphate is amphoteric, with basic behaviour predominating. |
| $\text{Na}_2\text{CO}_3$  | Sodium carbonate, <chem>[Na+].[Na+].[O-]C(=O)[O-]</chem>               | Carbonate accepts a proton from water.                                |
| $\text{NaHCO}_3$          | Sodium hydrogen carbonate, <chem>[Na+].OC(=O)[O-]</chem>               | Hydrogen carbonate is amphoteric, but its solution is mildly basic.   |

## G) Electronic formulas and bonding

### G(a) Sodium chlorate

The constituent ions are sodium ion  $[\text{Na}^+]$  and chlorate ion  $[\text{O}^-]\text{Cl}(=\text{O})=\text{O}$ .

Draw a separate sodium cation and a bracketed chlorate anion. In a conventional expanded-valence Lewis contributor:

- Chlorine is central and has one lone pair.
- Two oxygen atoms have double bonds to chlorine and two lone pairs each.
- The third oxygen has a single bond, three lone pairs, and formal charge  $-1$ .

There are three equivalent resonance contributors, obtained by exchanging the singly bonded oxygen. The ion is trigonal pyramidal. Bonding between the ions is ionic; bonding within chlorate is polar covalent. The SMILES records one contributor rather than the delocalized structure.

### G(b) Chloric acid

Chloric acid has SMILES OC1(=O)=O and conventional Lewis connectivity



Draw hydrogen bonded to oxygen, not directly to chlorine. Chlorine has one lone pair, and each oxygen has two lone pairs. All bonds within this molecular representation are polar covalent.

### G(c) Silicon tetrafluoride

Silicon tetrafluoride has SMILES F[Si](F)(F)F.

Draw silicon at the centre with four single bonds to fluorine. Each fluorine has three lone pairs; silicon has no lone pairs. The molecular geometry is tetrahedral, and the bonds are polar covalent. The tetrahedral geometry is not specified by the plain SMILES.

### G(d) Ammonia

Ammonia has SMILES N.

Draw three nitrogen–hydrogen single bonds and one lone pair on nitrogen. Four electron domains give a trigonal-pyramidal molecular geometry. The bonds are polar covalent.

### G(e) Calcium fluoride

Calcium fluoride has ionic formula-unit SMILES [Ca+2].[F-].[F-].

Draw one calcium ion, [Ca+2], and two separate fluoride ions, [F-]. Each fluoride has four lone pairs, completing its octet. The solid is an ionic lattice; it is not a discrete three-atom molecule.

### G(f) Water

Water has SMILES O.

Draw two oxygen–hydrogen single bonds and two lone pairs on oxygen. Its molecular geometry is bent, and its bonds are polar covalent.

### H) Structure of solid perchloric acid monohydrate

Perchloric acid, OC1(=O)(=O)=O, transfers a proton to water:



The solid is therefore formulated as **hydronium perchlorate**:



with formula-unit SMILES [OH3+].[O-]Cl(=O)(=O)=O.

Draw a trigonal-pyramidal hydronium cation, [OH3+], and a separate tetrahedral perchlorate anion, [O-]Cl(=O)(=O)=O. In the perchlorate ion, the four oxygen positions are equivalent and the bonding is delocalized over all four chlorine–oxygen connections.

In conventional Lewis notation, four equivalent contributors interchange the singly bonded, negatively charged oxygen. The displayed SMILES represents only one contributor. Hydrogen bonding between the ions is also absent from that notation.

This ionic formulation accounts for four equivalent chlorine–oxygen bonds without assigning one oxygen a distinct covalently attached acidic hydrogen.

### I) Hydrides of the second-period elements

The additional species needed here are:

| Substance                     | Name              | SMILES or qualified representation                                                  |
|-------------------------------|-------------------|-------------------------------------------------------------------------------------|
| LiH                           | Lithium hydride   | <chem>[Li+].[H-]</chem>                                                             |
| BeH <sub>2</sub>              | Beryllium hydride | <chem>[BeH2]</chem> , formula-unit representation only                              |
| B <sub>2</sub> H <sub>6</sub> | Diborane          | <chem>[H]1[BH2][H][BH2]1</chem> , schematic bridge-connectivity representation only |
| CH <sub>4</sub>               | Methane           | <chem>C</chem>                                                                      |
| HF                            | Hydrogen fluoride | <chem>F</chem>                                                                      |

Diborane has four terminal hydrogens and two bridging hydrogens. Each bridge forms a three-centre, two-electron bond involving two boron atoms and one hydrogen. The schematic string above must not be interpreted as eight ordinary two-centre, two-electron bonds; ordinary SMILES cannot faithfully encode this bonding.

**I(a)** The room-temperature solids are **lithium hydride and beryllium hydride**.

Lithium hydride forms an ionic lattice with strong electrostatic attractions. Beryllium hydride forms an extended covalent network, so melting or vaporization requires disruption of extensive bonding. The remaining hydrides are small molecular substances; under ordinary room conditions they are gases or, for water, a liquid.

**I(b) Lithium hydride** is ionic:



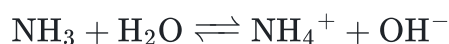
Its ions are lithium ion  $[\text{Li}^+]$  and hydride ion  $[\text{H}^-]$ .

**I(c) Beryllium hydride** is polymeric, conventionally written  $(\text{BeH}_2)_n$ . Beryllium is surrounded by bridging hydrogens in an extended network with electron-deficient multicentre bonding. The isolated formula-unit SMILES does not show that network.

Diborane is a discrete bridged molecule.

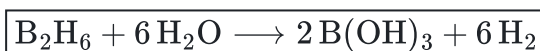
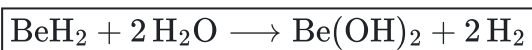
**I(d) Methane** does not react with water under normal conditions. Water itself is also unchanged on mixing with water, apart from its usual self-ionization equilibrium.

The other hydrides are reactive: lithium hydride, beryllium hydride and diborane undergo hydrolysis; ammonia and hydrogen fluoride participate in acid–base equilibria:



Hydroxide is  $[\text{OH}^-]$ , and fluoride is  $[\text{F}^-]$ .

**I(e)** The balanced reactions are:



The product identities are:

| Product                  | Name                | SMILES                                                      |
|--------------------------|---------------------|-------------------------------------------------------------|
| $\text{Be}(\text{OH})_2$ | Beryllium hydroxide | $\text{O}[\text{Be}]\text{O}$ , formula-unit representation |
| $\text{H}_2$             | Hydrogen            | $[\text{H}][\text{H}]$                                      |
| $\text{B}(\text{OH})_3$  | Boric acid          | $\text{OB}(\text{O})\text{O}$                               |
| $\text{LiBH}_4$          | Lithium borohydride | $[\text{Li}^+].[ \text{BH}_4^- ]$                           |

In the hydrolysis reactions, hydridic hydrogen combines with hydrogen from water to produce hydrogen gas. In the final reaction, hydride addition to diborane produces two tetrahedral borohydride ions,  $[\text{BH}_4^-]$ .

**I(f)** Removal of one proton gives:

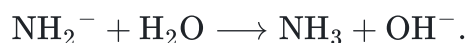
| Acid                 | Conjugate base  | Base name and SMILES           |
|----------------------|-----------------|--------------------------------|
| $\text{NH}_3$        | $\text{NH}_2^-$ | Amide ion, $[\text{NH}_2^-]$   |
| $\text{H}_2\text{O}$ | $\text{OH}^-$   | Hydroxide ion, $[\text{OH}^-]$ |

| Acid | Conjugate base | Base name and SMILES |
|------|----------------|----------------------|
| HF   | F <sup>-</sup> | Fluoride ion, [F-]   |

Acid strength increases from ammonia through water to hydrogen fluoride. Conjugate-base strength therefore decreases in that direction:

$$\boxed{\text{Increasing basic strength: } \text{F}^- < \text{OH}^- < \text{NH}_2^-}.$$

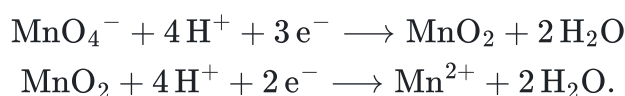
The amide ion is sufficiently basic to deprotonate water:



## J) Standard reduction potential

The relevant species are permanganate ion  $[\text{O}-][\text{Mn}](=\text{O})(=\text{O})=\text{O}$ , manganese(IV) oxide  $\text{O}=[\text{Mn}]=\text{O}$  as a formula-unit representation of its extended solid, and manganese(II) ion  $[\text{Mn}+2]$ .

The five-electron reduction is the sum of the three-electron and two-electron reductions:



Standard Gibbs energies are additive, with

$$\Delta G^0 = -nFE^0.$$

Therefore,

$$-5FE_1^0 = -3FE_2^0 - 2FE_3^0,$$

so

$$E_3^0 = \frac{5E_1^0 - 3E_2^0}{2}.$$

Substituting the supplied values:

$$E_3^0 = \frac{5(1.52) - 3(1.69)}{2} \text{ V} = \frac{7.60 - 5.07}{2} \text{ V} = 1.265 \text{ V}.$$

Thus

$$\boxed{E_3^0 \approx 1.27 \text{ V}}.$$

The solution was checked against the official solution.

## Problem 2: Composition of a CO-CO<sub>2</sub> mixture

In a gaseous mixture of CO and CO<sub>2</sub>, a mass ratio of carbon : oxygen = 1 : 2 was determined.

**2.1** Calculate the mass percent composition.

**2.2** Calculate the volume percent composition.

**2.3** Indicate values of the carbon: oxygen ratios for which both gases cannot be present simultaneously.

Official English text of the problem.

## Answers

- **2.1** Carbon monoxide, CO ( $[C-]\#[O+]$ ): **38.89 mass %**; carbon dioxide, CO<sub>2</sub> (O=C=O): **61.11 mass %**.
- **2.2** **50 volume %** CO and **50 volume %** CO<sub>2</sub>.
- **2.3** Defining  $r = m_C/m_O$ , both gases cannot be present simultaneously when

$$r \leq \frac{3}{8} \quad \text{or} \quad r \geq \frac{3}{4}.$$

Equality corresponds to a pure gas; values outside these bounds are impossible for a mixture containing only these two gases.

## Solution

### 2.1 Mass percent composition

Using the conventional atomic molar masses  $M(C) = 12 \text{ g mol}^{-1}$  and  $M(O) = 16 \text{ g mol}^{-1}$ ,

$$M(\text{CO}) = 28 \text{ g mol}^{-1}, \quad M(\text{CO}_2) = 44 \text{ g mol}^{-1}.$$

Let  $n_1$  and  $n_2$  be the amounts of CO and CO<sub>2</sub>, respectively. Each molecule contains one carbon atom, while their oxygen atom counts are one and two. Therefore,

$$\frac{m_C}{m_O} = \frac{(12 \text{ g mol}^{-1})(n_1 + n_2)}{(16 \text{ g mol}^{-1})(n_1 + 2n_2)} = \frac{1}{2}.$$

Consequently,

$$24(n_1 + n_2) = 16(n_1 + 2n_2) \implies n_1 = n_2.$$

On a basis of 1 mol of each gas, their masses are 28 g and 44 g, giving a total mass of 72 g. Thus,

$$w(\text{CO}) = \frac{28 \text{ g}}{72 \text{ g}} \times 100\% = \boxed{38.89\%},$$

$$w(\text{CO}_2) = \frac{44 \text{ g}}{72 \text{ g}} \times 100\% = \boxed{61.11\%}.$$

### 2.2 Volume percent composition

For ideal gases compared at the same temperature and pressure,  $V = nRT/P$ , so volume fractions equal mole fractions. Since  $n_1 = n_2$ ,

$$\varphi(\text{CO}) = \frac{n_1}{n_1 + n_2} = \frac{1}{2}, \quad \varphi(\text{CO}_2) = \frac{n_2}{n_1 + n_2} = \frac{1}{2}.$$

The composition is therefore

$$\boxed{50 \text{ volume \% CO} \quad \text{and} \quad 50 \text{ volume \% CO}_2}.$$

### 2.3 Ratios excluding simultaneous presence

Let  $x$  be the mole fraction of CO<sub>2</sub>. The carbon-to-oxygen mass ratio is

$$r = \frac{12}{16(1-x) + 32x} = \frac{3}{4(1+x)}.$$

Both gases are present only if  $0 < x < 1$ , which gives

$$\frac{3}{8} < r < \frac{3}{4}.$$

The endpoints correspond to:

- Pure  $\text{CO}_2$ :  $r = 12/32 = 3/8$ , or carbon : oxygen = 3 : 8.
- Pure  $\text{CO}$ :  $r = 12/16 = 3/4$ , or carbon : oxygen = 3 : 4.

Hence simultaneous presence is excluded for  $r \leq 3/8$  or  $r \geq 3/4$ . At either endpoint one component is absent; outside the interval even a pure gas or mixture of these two gases cannot reproduce the specified elemental ratio.

Equivalently, if carbon : oxygen is written 1 :  $a$ , simultaneous presence requires

$$\frac{4}{3} < a < \frac{8}{3},$$

and is excluded for  $a \leq 4/3$  or  $a \geq 8/3$ .

---

The solution was checked against the official solution.

### Problem 3: Analysis of a NaCl-KCl mixture with silver nitrate and a copper strip

A sample containing a mixture of sodium chloride and potassium chloride weights 25 g. After its dissolution in water 840 ml of  $\text{AgNO}_3$  solution ( $c = 0.5 \text{ mol dm}^{-3}$ ) is added. The precipitate is filtered off and a strip of copper weighing 100.00 g is dipped into the filtrate. After a given time interval the strip weights 101.52 g.

Calculate the mass percent composition of the mixture.

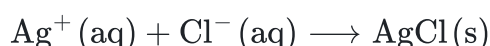
Official English text of the problem.

#### Answers

- **3.** Assuming complete reaction of the excess silver ions with copper, the mixture contains approximately **70% sodium chloride**,  $\text{NaCl}$ ,  $[\text{Na}^+] \cdot [\text{Cl}^-]$ , and **30% potassium chloride**,  $\text{KCl}$ ,  $[\text{K}^+] \cdot [\text{Cl}^-]$ , by mass.

#### Solution

**3.** Silver nitrate,  $\text{AgNO}_3$ ,  $[\text{Ag}^+] \cdot [\text{O}^-] [\text{N}^+] (= \text{O}) [\text{O}^-]$ , supplies silver(I) ions,  $\text{Ag}^+$ ,  $[\text{Ag}^+]$ . These precipitate chloride ions,  $\text{Cl}^-$ ,  $[\text{Cl}^-]$ , as silver chloride,  $\text{AgCl}$ ,  $[\text{Ag}^+] \cdot [\text{Cl}^-]$ :

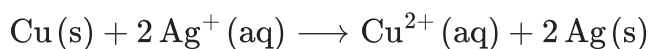


Each mole of either salt therefore consumes one mole of silver nitrate. The ionic SMILES specify composition; they do not depict the solid crystal lattices.

The amount of silver nitrate initially added is

$$n_0(\text{AgNO}_3) = (0.840 \text{ dm}^3)(0.5 \text{ mol dm}^{-3}) = 0.420 \text{ mol}.$$

After filtration, the excess silver ions react with copper,  $\text{Cu}$ ,  $[\text{Cu}]$ , producing copper(II) ions,  $\text{Cu}^{2+}$ ,  $[\text{Cu}^{2+}]$ , and depositing silver,  $\text{Ag}$ ,  $[\text{Ag}]$ :



The strip gains silver but loses copper. Thus its **net mass gain** is

$$\Delta m = 101.52 - 100.00 = 1.52 \text{ g}.$$

Using standard molar masses, since none are supplied,

$$\begin{aligned} M(\text{Ag}) &= 107.87 \text{ g mol}^{-1}, & M(\text{Cu}) &= 63.55 \text{ g mol}^{-1}, \\ M(\text{NaCl}) &= 58.44 \text{ g mol}^{-1}, & M(\text{KCl}) &= 74.55 \text{ g mol}^{-1}. \end{aligned}$$

If  $t$  moles of copper dissolve,  $2t$  moles of silver deposit:

$$\Delta m = t [2M(\text{Ag}) - M(\text{Cu})].$$

Hence

$$t = \frac{1.52 \text{ g}}{(2 \times 107.87 - 63.55) \text{ g mol}^{-1}} = 0.0099875 \text{ mol}.$$

Assuming all excess silver ions have reacted and the deposited silver remains on the strip,

$$n_{\text{excess}}(\text{Ag}^+) = 2t = 0.019975 \text{ mol}.$$

The amount of chloride originally present is therefore

$$n(\text{Cl}^-) = 0.420 - 0.019975 = 0.400025 \text{ mol}.$$

Let  $x = n(\text{NaCl})$  and  $y = n(\text{KCl})$ . The chloride balance and sample mass give

$$\begin{aligned} x + y &= 0.400025 \text{ mol}, \\ (58.44 \text{ g mol}^{-1})x + (74.55 \text{ g mol}^{-1})y &= 25 \text{ g}. \end{aligned}$$

Solving,

$$x \approx 0.29931 \text{ mol}, \quad y \approx 0.10072 \text{ mol}.$$

Consequently,

$$m(\text{NaCl}) \approx 17.49 \text{ g}, \quad m(\text{KCl}) \approx 7.51 \text{ g},$$

and the mass percentages are

$$w(\text{NaCl}) = \frac{17.49}{25} \times 100\% \approx 70\%$$

$$w(\text{KCl}) = \frac{7.51}{25} \times 100\% \approx 30\%$$

---

The solution was checked against the official solution.

## Problem 4: Kinetics and stereochemistry of the alkaline hydrolysis of

## chlorinated compounds

The following data were gathered for the alkaline hydrolysis of certain chlorinated compounds:

a) A certain volume of a solution of the neutral potassium salt of chlorosuccinic acid is mixed with an equal volume of hydroxide solution. The initial concentration of each solution is  $0.2 \text{ mol dm}^{-3}$ . The potassium hydroxide concentration in the reaction mixture was determined at different time intervals at  $25^\circ\text{C}$ . The following values were obtained:

| t (minutes)                          | 10    | 20    | 30    | 45    | 60    | 80    | 100   |
|--------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| $c(\text{KOH}) (\text{mol dm}^{-3})$ | 0.085 | 0.074 | 0.065 | 0.056 | 0.049 | 0.042 | 0.036 |

The experiment was repeated with the same initial solutions at  $35^\circ\text{C}$ . The hydroxide concentration is reduced to one half after 21 minutes.

b) In the hydrolysis of 3-chloro-3-methylhexane with potassium hydroxide, the concentration of potassium hydroxide was found to have been reduced to one half after 32 minutes at  $25^\circ\text{C}$  or 11 minutes at  $35^\circ\text{C}$ , regardless of the initial reactant concentrations (identical).

c) In the alkaline hydrolysis of 3-chloro-2,4-dimethyl-3-isopropylpentane an identical reaction mechanism as for reaction b was found but the reaction rate was about 100 times faster under the same reaction conditions.

Considering the above data answer the following questions:

**4.1** What is the reaction order in cases a, b, and c?

**4.2** What is the rate constant at  $25^\circ\text{C}$  for reaction a? Indicate the units.

**4.3** Calculate the activation energies for reactions a and b.

**4.4** If in reaction a dipotassium salt of L-chlorosuccinic acid (which is levorotatory,) is used, what type of optical rotation will be exhibited by the corresponding salt of malic acid formed by hydrolysis?

**4.5** If the levorotatory isomer is also used in reaction b, what optical rotation will be exhibited by 3-methyl-3-hexanol formed in the hydrolysis reaction?

**4.6** Why is the rate of reaction c much faster than that of reaction b when both reactions are of the same type and occur under the same temperature and concentration conditions?

Official English text of the problem.

## Answers

- 4.1: a: second order; b: first order; c: first order.** The intended mechanisms are  $S_N2$ ,  $S_N1$ , and  $S_N1$ , respectively.
- 4.2:**  $k_{a,25} \approx 0.175 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ .
- 4.3:**  $E_{a,a} \approx 76 \text{ kJ mol}^{-1}$ ;  $E_{a,b} \approx 82 \text{ kJ mol}^{-1}$ .

- **4.4:** Inversion gives **dipotassium D-malate**,  $[K^+] \cdot [K^+] \cdot O=C([O^-])[C@H](O)CC(=O)[O^-]$ . **Dextrorotatory** is the likely intended answer, but the rotation sign does not follow from configurational inversion alone; it requires an empirical assignment for the product salt.
- **4.5: Optically inactive racemic 3-methylhexan-3-ol**, an equimolar mixture of  $CC[C@](C)(O)CCC$  and  $CC[C@@](C)(O)CCC$ ; net rotation is zero in the ideal  $S_N1$  model.
- **4.6:** The three bulky isopropyl groups in **c** cause substantial steric strain. Ionization toward a planar carbocation relieves this strain, lowering the activation barrier and accelerating the reaction.

## Solution

### 4.1 — Reaction orders

Each substitution consumes one hydroxide ion,  $OH^-$ ,  $[OH^-]$ , per organic chloride and releases one chloride ion,  $Cl^-$ ,  $[Cl^-]$ .

For **a**, mixing equal volumes halves both initial concentrations:

$$c_0 = \frac{0.2V}{2V} = 0.10 \text{ mol dm}^{-3}.$$

Because the reactants begin at equal concentrations and are consumed in a 1 : 1 ratio, their concentrations remain equal. Denote either concentration by  $c$ .

For the proposed bimolecular substitution,

$$v = k_a[\text{chlorosuccinate}][OH^-],$$

so along this equimolar reaction mixture,

$$-\frac{dc}{dt} = k_a c^2.$$

Integration gives

$$\boxed{\frac{1}{c} - \frac{1}{c_0} = k_a t}.$$

The experimental values give an approximately constant value of  $(1/c - 1/c_0)/t$ , as calculated in 4.2. Thus **a is second order overall**, consistent with an  $S_N2$  substitution.

For **b**, the half-life is independent of the initial concentration. This is characteristic of first-order kinetics:

$$-\frac{dc}{dt} = k_b c, \quad c = c_0 e^{-k_b t}, \quad \boxed{t_{1/2} = \frac{\ln 2}{k_b}}.$$

Equal initial concentrations and 1 : 1 consumption mean that halving the hydroxide concentration also corresponds to halving the organic chloride concentration. The tertiary chloride structure supports an  $S_N1$  mechanism, with slow unimolecular ionization:

$$v = k_b[\text{organic chloride}].$$

Thus **b is first order**, with no hydroxide concentration factor in the ideal rate law.

Since **c** has the same mechanism as **b**, it is also **first order**.

#### 4.2 — Rate constant for a at 25 °C

Using  $c_0 = 0.10 \text{ mol dm}^{-3}$ ,

$$k_a = \frac{1/c - 1/c_0}{t}.$$

The individual estimates are:

| $t / \text{min}$                                      | 10     | 20     | 30     | 45     | 60     | 80     | 100    |
|-------------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|
| $k_a / \text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ | 0.1765 | 0.1757 | 0.1795 | 0.1746 | 0.1735 | 0.1726 | 0.1778 |

For example, at 45 minutes,

$$k_a = \frac{1/0.056 - 1/0.100}{45} = 0.1746 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}.$$

Fitting  $1/c - 1/c_0 = k_a t$  to all seven measurements gives approximately  $0.17546 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ . Accordingly,

$$k_{a,25} \approx 0.175 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}.$$

The corresponding half-life is approximately

$$t_{1/2,a,25} = \frac{1}{k_{a,25}c_0} \approx 57 \text{ min},$$

consistent with the measured concentration being just below half its initial value at 60 minutes.

#### 4.3 — Activation energies

The two-temperature Arrhenius equation is

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Use

$$T_1 = 298.15 \text{ K}, \quad T_2 = 308.15 \text{ K}, \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

For **reaction a**, the equimolar second-order half-life satisfies

$$t_{1/2} = \frac{1}{kc_0}.$$

Hence, at 35 °C,

$$k_{a,35} = \frac{1}{(0.10 \text{ mol dm}^{-3})(21 \text{ min})} = 0.47619 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}.$$

Using the unrounded fitted value at 25 °C,

$$E_{a,a} = \frac{8.314 \ln(0.47619/0.17546)}{1/298.15 - 1/308.15} \text{ J mol}^{-1} \approx 7.63 \times 10^4 \text{ J mol}^{-1}.$$

Thus,

$$E_{a,a} \approx 76 \text{ kJ mol}^{-1}.$$

For **reaction b**,

$$k_{b,25} = \frac{\ln 2}{32 \text{ min}} = 0.02166 \text{ min}^{-1},$$

$$k_{b,35} = \frac{\ln 2}{11 \text{ min}} = 0.06301 \text{ min}^{-1}.$$

Therefore,

$$\frac{k_{b,35}}{k_{b,25}} = \frac{32}{11},$$

and

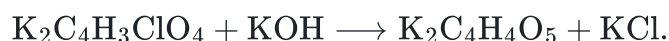
$$E_{a,b} = \frac{8.314 \ln(32/11)}{1/298.15 - 1/308.15} \text{ J mol}^{-1} \approx 8.16 \times 10^4 \text{ J mol}^{-1}.$$

Thus,

$$E_{a,b} \approx 82 \text{ kJ mol}^{-1}.$$

#### 4.4 — Stereochemistry of chlorosuccinate hydrolysis

Potassium hydroxide has SMILES `[K+] . [OH-]`, and potassium chloride has SMILES `[K+] . [Cl-]`. The balanced hydrolysis is

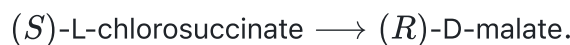


The organic reactant and product are:

- **Dipotassium L-chlorosuccinate**, with the usual L assignment corresponding here to *S*: `[K+] . [K+] . O=C([O-])[C@H](Cl)CC(=O)[O-]`.
- **Dipotassium D-malate**, corresponding here to *R*: `[K+] . [K+] . O=C([O-])[C@H](O)CC(=O)[O-]`.

In an  $S_N2$  reaction, a lone pair on hydroxide oxygen attacks the stereogenic carbon from the side opposite the carbon–chlorine bond. Carbon–oxygen bond formation and carbon–chlorine bond cleavage occur together, with the latter bond's electron pair passing to chlorine.

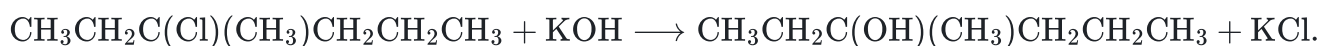
This produces **Walden inversion**. Here the substituent-priority ordering remains analogous after chlorine is replaced by hydroxyl, so



The likely intended elementary answer is that the product is **dextrorotatory**. However, this requires an additional empirical identification of the product salt as the positive-rotation enantiomer under the measurement conditions. Neither *R/S* nor D/L notation determines the sign of optical rotation, and replacing chlorine by hydroxyl produces a different compound. Consequently, **the supplied information establishes configurational inversion, but does not by itself establish a positive rotation**.

#### 4.5 — Stereochemistry of 3-chloro-3-methylhexane hydrolysis

The balanced substitution is



The starting material is **3-chloro-3-methylhexane**. Its two enantiomers are CC[C@](C)(Cl)CCC and CC[C@@](C)(Cl)CCC; the designation "levorotatory" alone does not identify which absolute configuration is present.

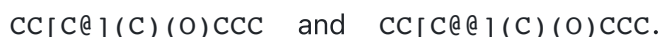
Slow ionization produces the **3-methylhexan-3-yl carbocation**, CC[C+](C)CCC:



The positively charged carbon is approximately trigonal planar. In the ideal freely solvated carbocation model, hydroxide attacks either face with equal probability:



The product is therefore **racemic 3-methylhexan-3-ol**, containing equal amounts of



These enantiomers have equal and opposite rotations under identical conditions. Thus,

$$\boxed{\alpha_{\text{mixture}} = 0},$$

and the product is **optically inactive by external compensation**.

#### 4.6 — Why c reacts much faster

The substrate in c, **3-chloro-2,4-dimethyl-3-isopropylpentane**, has SMILES CC(C)C(Cl)(C(C)C)C(C)C. Its chlorine-bearing carbon is attached to **three isopropyl groups**.

The formal substitution product is **2,4-dimethyl-3-(propan-2-yl)pentan-3-ol**, CC(C)C(O)(C(C)C)C(C)C:



The rate-determining ionization develops the **tris(propan-2-yl)methyl carbocation**, CC(C)[C+](C(C)C)C(C)C.

In the starting chloride, three bulky isopropyl groups crowd around a tetrahedral carbon. As the carbon–chlorine bond breaks, the central carbon approaches a trigonal planar geometry, with angles between its three carbon substituents approaching  $120^\circ$ . This change relieves substantial steric strain.

Reaction b has methyl, ethyl, and propyl groups around the reacting carbon and experiences less such crowding. Consequently, ionization in c gains more from strain relief and has a lower activation barrier. This **steric acceleration of the  $S_N1$  ionization** explains its much greater rate.

The solution was checked against the official solution.

## Problem 5: Ethanol dehydration equilibrium and its pressure dependence

On passing ethanol over a catalyst at 400 K, a dehydration reaction occurs resulting in the formation of ethylene:



At the above temperature and  $p_0 = 101.325 \text{ kPa}$ , the conversion of ethyl alcohol is 90.6 mol %.

**5.1** Calculate the equilibrium constant  $K_p$  of the reaction under given conditions.

**5.2** Calculate the values of the equilibrium constants  $K_x$  and  $K_c$  at the above temperature.

**5.3** Calculate the ethanol conversion at the following pressures:

$5p_0$ ,  $10p_0$ ,  $50p_0$ ,  $100p_0$ , and  $200p_0$ .

**5.4** Plot the graph for the variation of conversion vs. pressure.

Official English text of the problem.

## Answers

The constants below use the unnormalized pressure and concentration quotients defined in the solution.

- 5.1**  $K_p = 4.64 \times 10^2 \text{ kPa} = 4.58 \text{ atm}$ .
- 5.2** At  $p = p_0$ ,  $K_x = 4.58$ ; at 400 K,  $K_c = 0.140 \text{ mol L}^{-1}$ .
- 5.3** The equilibrium conversions at  $5p_0$ ,  $10p_0$ ,  $50p_0$ ,  $100p_0$ ,  $200p_0$  are, respectively, 69.1%, 56.1%, 29.0%, 20.9%, 15.0%.
- 5.4** Plot

$$\text{Conversion (\%)} = 100 \sqrt{\frac{4.58148}{4.58148 + p/p_0}}.$$

The curve decreases smoothly and is convex upwards, approaching 100% as  $p \rightarrow 0^+$  and 0% as  $p \rightarrow \infty$ .

## Solution

### 5.1 — Pressure equilibrium constant

The balanced equilibrium is



The species are ethanol (CCO), ethylene, also called ethene (C=C), and water (O).

Assume a pure ethanol feed, ideal-gas behavior, and that the stated pressures are total equilibrium pressures. Let  $\alpha$  be the fraction of the initial ethanol converted. Starting with 1 mol of ethanol gives:

| Species  | Equilibrium amount (mol) | Mole fraction                   |
|----------|--------------------------|---------------------------------|
| Ethanol  | $1 - \alpha$             | $\frac{1 - \alpha}{1 + \alpha}$ |
| Ethylene | $\alpha$                 | $\frac{\alpha}{1 + \alpha}$     |
| Water    | $\alpha$                 | $\frac{\alpha}{1 + \alpha}$     |
| Total    | $1 + \alpha$             | 1                               |

Since  $p_i = x_i p$ , the pressure quotient is

$$K_p = \frac{p_{\text{C}_2\text{H}_4} p_{\text{H}_2\text{O}}}{p_{\text{C}_2\text{H}_5\text{OH}}} = \frac{\left(\frac{\alpha p}{1 + \alpha}\right)^2}{\frac{(1 - \alpha)p}{1 + \alpha}} = \frac{\alpha^2 p}{1 - \alpha^2}.$$

At  $p = p_0 = 101.325 \text{ kPa}$ , the conversion is  $\alpha_0 = 0.906$ . Thus

$$K_p = \frac{0.906^2}{1 - 0.906^2} (101.325 \text{ kPa}) = 464.218 \text{ kPa}.$$

Therefore,

$$\boxed{K_p = 464 \text{ kPa} = 4.58 \text{ atm}}.$$

## 5.2 — Mole-fraction and concentration equilibrium constants

The mole-fraction quotient is

$$K_x = \frac{x_{\text{C}_2\text{H}_4} x_{\text{H}_2\text{O}}}{x_{\text{C}_2\text{H}_5\text{OH}}} = \frac{\alpha^2}{1 - \alpha^2}.$$

At the specified reference pressure,

$$K_x(p_0) = \frac{0.906^2}{1 - 0.906^2} = 4.58148,$$

so

$$\boxed{K_x(p_0) = 4.58}.$$

Here  $K_x$  depends on total pressure: at fixed temperature,

$$K_x(p) = \frac{K_p}{p}.$$

For the concentration quotient,

$$K_c = \frac{c_{\text{C}_2\text{H}_4} c_{\text{H}_2\text{O}}}{c_{\text{C}_2\text{H}_5\text{OH}}}.$$

The change in the number of gaseous moles is

$$\Delta\nu = (1 + 1) - 1 = 1.$$

Using  $p_i = c_i RT$ ,

$$K_p = K_c (RT)^{\Delta\nu} = K_c RT.$$

With  $R = 8.31446 \text{ kPa L mol}^{-1} \text{ K}^{-1}$ ,

$$K_c = \frac{464.218 \text{ kPa}}{(8.31446 \text{ kPa L mol}^{-1} \text{ K}^{-1})(400 \text{ K})} = 0.139582 \text{ mol L}^{-1}.$$

Hence

$$\boxed{K_c = 0.140 \text{ mol L}^{-1}}.$$

## 5.3 — Conversion at the specified pressures

At constant temperature,  $K_p$  remains unchanged. Rearranging

$$K_p = \frac{\alpha^2 p}{1 - \alpha^2}$$

gives

$$K_p = \alpha^2(K_p + p), \quad \alpha = \sqrt{\frac{K_p}{K_p + p}}.$$

Writing  $r = p/p_0$ , and using  $K_p/p_0 = 4.58148$ ,

$$\alpha(r) = \sqrt{\frac{4.58148}{4.58148 + r}}.$$

The resulting conversions are:

| Pressure | Pressure (kPa) | Ethanol conversion (mol %) |
|----------|----------------|----------------------------|
| $5p_0$   | 506.625        | 69.1                       |
| $10p_0$  | 1013.25        | 56.1                       |
| $50p_0$  | 5066.25        | 29.0                       |
| $100p_0$ | 10132.5        | 20.9                       |
| $200p_0$ | 20265          | 15.0                       |

The forward reaction converts one mole of gas into two. Increasing pressure therefore favors ethanol and reduces its equilibrium conversion.

#### 5.4 — Description of the graph

Use total pressure  $p/p_0$  on the horizontal axis, from 0 to 200, and ethanol conversion in mol % on the vertical axis, from 0 to 100.

Draw the smooth curve

$$y = 100 \sqrt{\frac{4.58148}{4.58148 + p/p_0}}$$

through the reference point (1, 90.6) and the five calculated points:

$$(5, 69.1), \quad (10, 56.1), \quad (50, 29.0), \quad (100, 20.9), \quad (200, 15.0).$$

The curve approaches (0, 100) as pressure tends to zero. It falls steeply at low pressure and progressively flattens; it is convex upwards throughout. At indefinitely increasing pressure, conversion approaches zero asymptotically.

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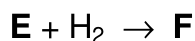
The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

## Problem 6: Identification of compounds A-G from a base-catalysed reaction sequence

One mole of compound **A** reacts successively with 3 moles of compound **B** in aqueous solution in the presence of a basic catalyst (such as  $\text{Ca}(\text{OH})_2$ ):



Hydrogenation of compound **E** yields compound **F**:



**F** has the composition: C = 44.18 %, H = 8.82 %, O = 47.00 %.

Its molar mass:  $M = 136 \text{ g mol}^{-1}$

Knowing that 13.6 g of **F** reacts with 40.8 g acetic anhydride to form product **G** and acetic acid write down all chemical equations and assign the letters **A**, **B**, **C**, **D**, **E**, **F**, and **G** to particular formulas of compounds.

Official English text of the problem.

## Answers

- **Problem 6** — no numbered subparts or point values are printed.

| Compound | Name and condensed structural formula                                                                                            | SMILES                                               |
|----------|----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|
| <b>A</b> | Ethanal (acetaldehyde), $\text{CH}_3\text{CHO}$                                                                                  | <chem>CC=O</chem>                                    |
| <b>B</b> | Methanal (formaldehyde), $\text{HCHO}$                                                                                           | <chem>C=O</chem>                                     |
| <b>C</b> | 3-Hydroxypropanal, $\text{HOCH}_2\text{CH}_2\text{CHO}$                                                                          | <chem>O=CCCO</chem>                                  |
| <b>D</b> | 3-Hydroxy-2-(hydroxymethyl)propanal, $(\text{HOCH}_2)_2\text{CHCHO}$                                                             | <chem>O=CC(CO)CO</chem>                              |
| <b>E</b> | 3-Hydroxy-2,2-bis(hydroxymethyl)propanal (pentaerythrose), $(\text{HOCH}_2)_3\text{CCHO}$                                        | <chem>O=CC(CO)(CO)CO</chem>                          |
| <b>F</b> | Pentaerythritol, $\text{C}(\text{CH}_2\text{OH})_4$ , molecular formula $\text{C}_5\text{H}_{12}\text{O}_4$                      | <chem>C(CO)(CO)(CO)CO</chem>                         |
| <b>G</b> | Pentaerythritol tetraacetate, $\text{C}(\text{CH}_2\text{OCOCH}_3)_4$ , molecular formula $\text{C}_{13}\text{H}_{20}\text{O}_8$ | <chem>C(COC(C)=O)(COC(C)=O)(COC(C)=O)COC(C)=O</chem> |

All seven compounds are achiral. The balanced equations are developed below in the order of the reaction sequence.

## Solution

### Determining the molecular formula and hydroxyl content of **F**.

Write the molecular formula as  $\text{C}_x\text{H}_y\text{O}_z$ . Using atomic molar masses of 12, 1, and  $16 \text{ g mol}^{-1}$ , respectively,

$$x = \frac{0.4418(136 \text{ g mol}^{-1})}{12 \text{ g mol}^{-1}} = 5.007 \approx 5,$$

$$y = \frac{0.0882(136 \text{ g mol}^{-1})}{1 \text{ g mol}^{-1}} = 11.995 \approx 12,$$

$$z = \frac{0.4700(136 \text{ g mol}^{-1})}{16 \text{ g mol}^{-1}} = 3.995 \approx 4.$$

Thus **F** has molecular formula  $\boxed{\text{C}_5\text{H}_{12}\text{O}_4}$ , whose calculated molar mass is  $136 \text{ g mol}^{-1}$ .

Acetic anhydride,  $\text{CC}(=\text{O})\text{OC}(\text{C})=\text{O}$ , has formula  $\text{C}_4\text{H}_6\text{O}_3$  and molar mass

$$M = 4(12) + 6(1) + 3(16) = 102 \text{ g mol}^{-1}.$$

The reacting amounts are therefore

$$n(\mathbf{F}) = \frac{13.6 \text{ g}}{136 \text{ g mol}^{-1}} = 0.100 \text{ mol},$$

$$n(\text{acetic anhydride}) = \frac{40.8 \text{ g}}{102 \text{ g mol}^{-1}} = 0.400 \text{ mol}.$$

Hence one mole of **F** consumes four moles of acetic anhydride. Each alcohol hydroxyl group consumes one anhydride molecule during acetylation, producing one ester group and one molecule of acetic acid,  $\text{CC}(=\text{O})\text{O}$ . Consequently, **F contains four hydroxyl groups**, accounting for all four oxygen atoms.

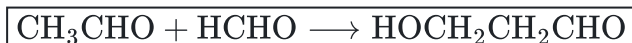
### Identifying A and B.

The aqueous basic conditions and successive additions indicate crossed aldol additions. In these reactions, methanal supplies a hydroxymethyl group,  $-\text{CH}_2\text{OH}$ , while the original aldehyde group remains available for the final hydrogenation.

Three additions of one-carbon methanal to a five-carbon final skeleton leave two carbons in **A**. The required two-carbon aldehyde is ethanal. Its methyl group has exactly three hydrogens on the carbon adjacent to the aldehyde group, allowing three successive hydroxymethylations.

Thus **A is ethanal** and **B is methanal**. The first three equations below are base-catalysed; calcium hydroxide,  $[\text{Ca}+2] \cdot [\text{OH}-] \cdot [\text{OH}-]$ , is the example given in the problem.

### First addition: $\mathbf{A + B \rightarrow C}$ .



One hydrogen on ethanal's methyl carbon is replaced by a hydroxymethyl group. The product is **C**, 3-hydroxypropanal.

### Second addition: $\mathbf{C + B \rightarrow D}$ .



The carbon adjacent to the aldehyde group still has two hydrogens. A second hydroxymethylation gives **D**, 3-hydroxy-2-(hydroxymethyl)propanal.

### Third addition: $\mathbf{D + B \rightarrow E}$ .



The last hydrogen on that carbon is replaced, giving **E**, pentaerythrose, with molecular formula  $C_5H_{10}O_4$ . Its central carbon now bears three hydroxymethyl groups and one aldehyde group. It has no remaining hydrogen adjacent to the aldehyde group, so this sequence of aldol additions stops.

These are addition reactions: no small molecule is eliminated.

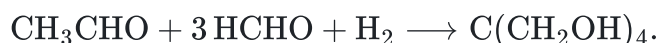
#### Hydrogenation: E → F.

Hydrogen,  $[H][H]$ , reduces the remaining aldehyde group to a fourth hydroxymethyl group:



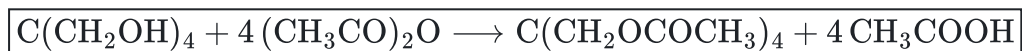
The product **F** is therefore **pentaerythritol**, a central carbon bonded to four identical  $-CH_2OH$  groups. This agrees with both its molecular formula and its four acetyltable hydroxyl groups.

The overall synthesis through hydrogenation is

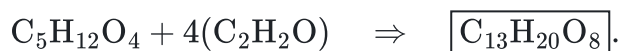


#### Acetylation: F → G.

All four hydroxyl groups undergo acetylation:



Thus **G** is **pentaerythritol tetraacetate**. Each hydroxyl hydrogen is replaced by an acetyl group, giving a net addition of  $C_2H_2O$  per hydroxyl group. Its molecular formula is consequently

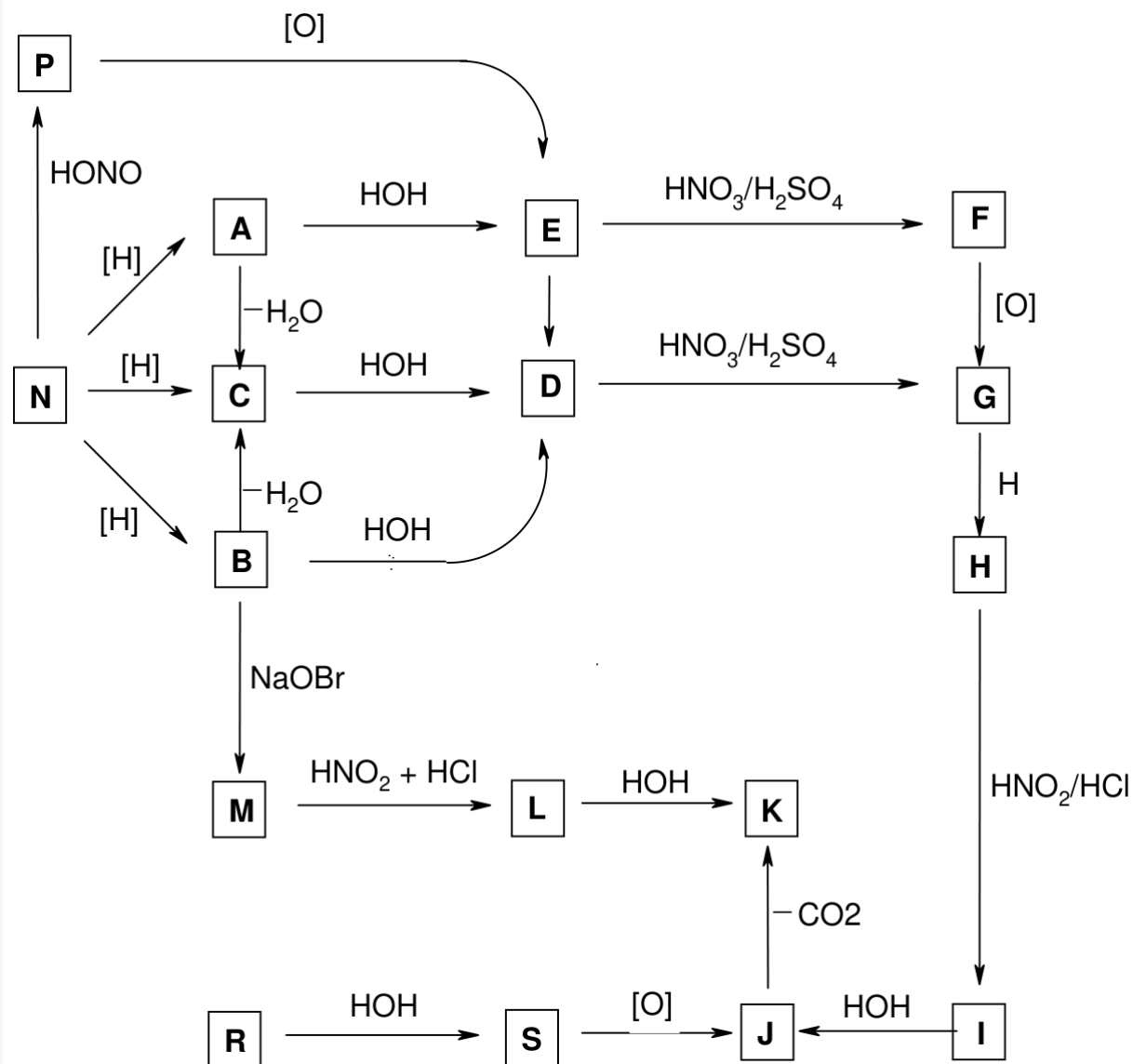



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The solution was checked against the official solution.

## Problem 7: Reaction scheme of the isomers A and B ( $C_7H_7NO$ ): compounds A-S

Knowing that compounds **A** and **B** are isomers with the molecular formula  $C_7H_7NO$  and the relative molecular mass of compound **M** is 93, determine the formulae of compounds **A** to **S** taking in account the reactions given in the following reaction scheme:



Official English text of the problem.

## Answers

7. The assignments are given below. They require reversing the three reduction arrows adjoining *N*. The *R*, *S* pair is one chemically sound completion of that branch.

| Compound | Name                                 | Formula      | SMILES                                 |
|----------|--------------------------------------|--------------|----------------------------------------|
| A        | Benzaldehyde oxime<br>(benzaldoxime) | $C_7H_7NO$   | <chem>ON=Cc1ccccc1</chem>              |
| B        | Benzamide                            | $C_7H_7NO$   | <chem>NC(=O)c1ccccc1</chem>            |
| C        | Benzonitrile                         | $C_7H_5N$    | <chem>N#Cc1ccccc1</chem>               |
| D        | Benzoic acid                         | $C_7H_6O_2$  | <chem>O=C(O)c1ccccc1</chem>            |
| E        | Benzaldehyde                         | $C_7H_6O$    | <chem>O=Cc1ccccc1</chem>               |
| F        | 3-Nitrobenzaldehyde                  | $C_7H_5NO_3$ | <chem>O=Cc1cccc([N+](=O)[O-])c1</chem> |

| Compound | Name                               | Formula                 | SMILES                                      |
|----------|------------------------------------|-------------------------|---------------------------------------------|
| G        | 3-Nitrobenzoic acid                | $C_7H_5NO_4$            | <chem>O=C(O)c1cccc([N+](=O)[O-])c1</chem>   |
| H        | 3-Aminobenzoic acid                | $C_7H_7NO_2$            | <chem>Nc1cccc(C(=O)O)c1</chem>              |
| I        | 3-Carboxybenzenediazonium chloride | $[C_7H_5N_2O_2]^+ Cl^-$ | <chem>O=C(O)c1cccc([N+]=[N])c1.[Cl-]</chem> |
| J        | 3-Hydroxybenzoic acid              | $C_7H_6O_3$             | <chem>O=C(O)c1cccc(O)c1</chem>              |
| K        | Phenol                             | $C_6H_6O$               | <chem>Oc1ccccc1</chem>                      |
| L        | Benzenediazonium chloride          | $[C_6H_5N_2]^+ Cl^-$    | <chem>N#[N+]c1ccccc1.[Cl-]</chem>           |
| M        | Aniline                            | $C_6H_7N$               | <chem>Nc1ccccc1</chem>                      |
| N        | Benzylamine                        | $C_7H_9N$               | <chem>NCc1ccccc1</chem>                     |
| P        | Benzyl alcohol                     | $C_7H_8O$               | <chem>OCc1ccccc1</chem>                     |
| R        | 3-Formylbenzenediazonium chloride  | $[C_7H_5N_2O]^+ Cl^-$   | <chem>O=Cc1cccc([N+]=[N])c1.[Cl-]</chem>    |
| S        | 3-Hydroxybenzaldehyde              | $C_7H_6O_2$             | <chem>O=Cc1cccc(O)c1</chem>                 |

The scheme contains no compounds labelled *O* or *Q*. The configuration about the oxime double bond in *A* is unspecified; its SMILES therefore leaves *E/Z* stereochemistry unassigned.

## Solution

7. The names and structures of the compounds are listed above. In the equations below, every disubstituted benzene ring has its substituents in the **1,3-positions**. The symbols [H] and [O] denote formal reducing and oxidizing equivalents, respectively. Hydrolyses are written as balanced overall equations with neutral products; acid/base conditions and workup are implicit where needed.

### Identifying *B* and the $M \rightarrow L \rightarrow K$ branch.

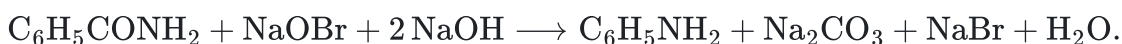
The reaction of *B* with sodium hypobromite identifies the **Hofmann rearrangement** of a primary amide. Its carbonyl carbon is lost, while its remaining organic group becomes attached to the amino group.

Starting from  $C_7H_7NO$ , the resulting amine has formula  $C_6H_7N$ :

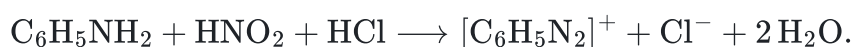
$$M_r = 6(12) + 7(1) + 14 = 93.$$

Relative molecular mass is dimensionless. This matches the stated value. Together with the aromatic reactions elsewhere in the scheme, this identifies *M* as **aniline** and *B* as **benzamide**.

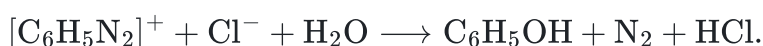
The balanced equation under alkaline conditions is



Aniline undergoes diazotization in cold hydrochloric acid, giving *L*, **benzenediazonium chloride**:



Warming the diazonium salt with water replaces the diazonium group by a hydroxyl group, giving *K*, **phenol**:

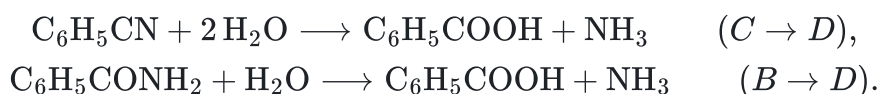


Identifying *A*, *C*, *D*, *E*.

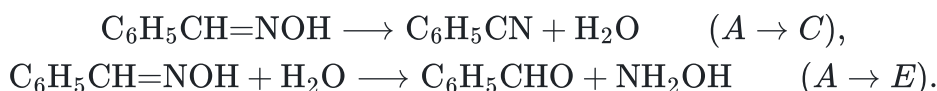
Dehydration of benzamide gives *C*, **benzonitrile**:



Hydrolysis of either the nitrile or the amide gives *D*, **benzoic acid**:



The isomer *A*, which also loses water to form benzonitrile but hydrolyses to a different compound, is **benzaldehyde oxime**. Its dehydration and hydrolysis are



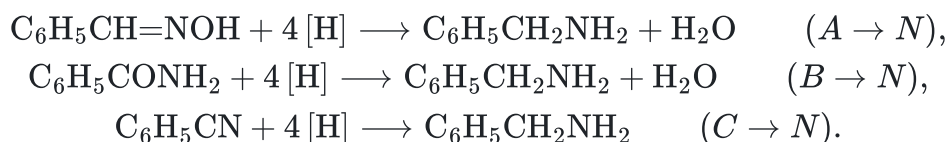
Here the nitrogen-containing hydrolysis product is hydroxylamine, NO. Thus *E* is **benzaldehyde**. The unlabelled  $E \rightarrow D$  transformation is oxidation:



Identifying *N*, *P* and resolving the reduction arrows.

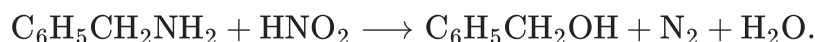
Reduction of an aldoxime, a nitrile, or a primary amide gives the corresponding primary amine.

Consequently, *A*, *B*, *C* all give *N*, **benzylamine**:



These reactions require the reverse of the directions printed beside *N*.

Benzylamine reacts with nitrous acid to give *P*, **benzyl alcohol**, with evolution of nitrogen:

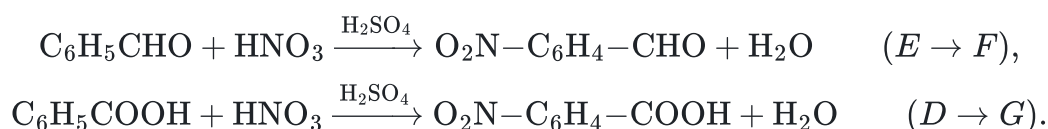


Controlled oxidation of benzyl alcohol produces benzaldehyde, confirming the connection  $P \rightarrow E$ :

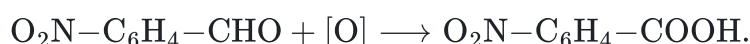


Identifying *F*, *G*, *H*, *I*, *J*.

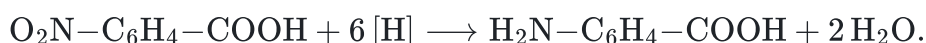
Both the aldehyde group and the carboxyl group are **meta-directing** in electrophilic aromatic substitution. Accordingly, the principal mononitration products are *F*, **3-nitrobenzaldehyde**, and *G*, **3-nitrobenzoic acid**:



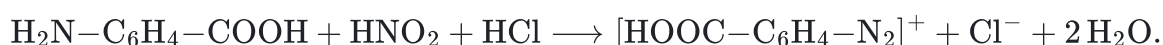
Oxidation of the aldehyde group in *F* gives the same acid *G*:



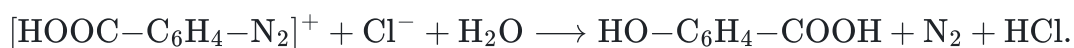
Selective reduction of the nitro group gives *H*, **3-aminobenzoic acid**:



Diazotization gives *I*, **3-carboxybenzenediazonium chloride**:



Hydrolysis of this diazonium salt gives *J*, **3-hydroxybenzoic acid**:



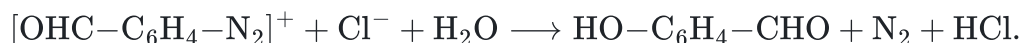
Decarboxylation gives phenol, agreeing with the independently established identity of *K*:



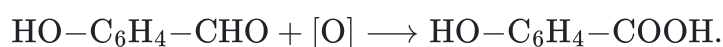
This last equation expresses the overall transformation; suitable alkaline decarboxylation conditions followed by acidification can be used.

**Completing  $R \rightarrow S \rightarrow J$  with standard reactions.**

Choose *R* as **3-formylbenzenediazonium chloride**. Its hydrolysis gives *S*, **3-hydroxybenzaldehyde**, by the same diazonium-to-phenol transformation used in the other branches:



A mild, aldehyde-selective oxidation then gives *J*:



For example, silver(I) oxidation followed by acidic workup accomplishes this transformation. Its overall stoichiometry can be represented as



The readily oxidized aldehyde group allows mild conditions that preserve the phenolic group. Thus both steps in this proposed branch are standard transformations.

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