

IChO 2003

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Problem 1: Solubility of thorium iodate

SECTION A: General Chemistry

QUESTION 1

The molar solubility s (mol dm^{-3}) of $\text{Th}(\text{IO}_3)_4$ as a function of the solubility product K_{sp} of this sparingly soluble thorium salt is given by the equation:

(a) $s = (K_{sp}/128)^{1/4}$ ☐

(b) $s = (K_{sp}/256)^{1/5}$ ☐

(c) $s = 256 K_{sp}^{1/4}$ ☐

(d) $s = (128 K_{sp})^{1/4}$ ☐

(e) $s = (256 K_{sp})^{1/5}$ ☐

(f) $s = (K_{sp}/128)^{1/5}/2$ ☐

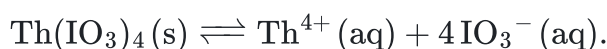
Official English text of the problem.

Answers

- 1. (b) ☐ $s = \left(\frac{K_{sp}}{256} \right)^{1/5}$. Mark only the box beside (b).

Solution

1. Thorium(IV) iodate dissolves according to



The dissolved ions are the thorium(IV) ion, $[\text{Th}^{4+}]$, and the iodate ion, $[\text{O}-]\text{I}(=\text{O})=\text{O}$. The iodate SMILES represents one resonance form; it does not encode the ion's trigonal pyramidal geometry.

For a molar solubility s , each mole of salt supplies one mole of thorium(IV) ions and four moles of iodate ions. Thus, with concentrations expressed in mol dm^{-3} ,

$$[\text{Th}^{4+}] = s, \quad [\text{IO}_3^{-}] = 4s.$$

Using the concentration form of the solubility product, with the pure solid omitted,

$$K_{sp} = [\text{Th}^{4+}][\text{IO}_3^-]^4 = s(4s)^4 = 256s^5.$$

Rearranging,

$$s = \left(\frac{K_{sp}}{256} \right)^{1/5},$$

which is **option (b)**.

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

Problem 2: Exact hydrogen ion concentration of hydrochloric acid

Which one of the following equations must be used for the exact calculation of $[\text{H}^+]$ of an aqueous HCl solution at any concentration c_{HCl} ? ($K_w = 1 \times 10^{-14}$).

- (a) $[\text{H}^+] = c_{\text{HCl}}$ ()
- (b) $[\text{H}^+] = c_{\text{HCl}} + K_w/[\text{H}^+]$ ()
- (c) $[\text{H}^+] = c_{\text{HCl}} + K_w$ ()
- (d) $[\text{H}^+] = c_{\text{HCl}} - K_w/[\text{H}^+]$ ()

Official English text of the problem.

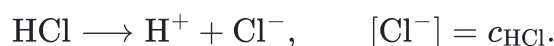
Answers

- **2: (b)**. Mark only the box beside

$$[\text{H}^+] = c_{\text{HCl}} + \frac{K_w}{[\text{H}^+]}.$$

Solution

2. In the model assumed by the problem, hydrogen chloride HCl dissociates completely into hydrogen ions (protons) $[\text{H}^+]$ and chloride ions $[\text{Cl}^-]$. Using the problem's aqueous H^+ notation,



Water H_2O also undergoes autoionization, producing hydrogen ions and hydroxide ions $[\text{OH}^-]$:



Thus,

$$K_w = [\text{H}^+][\text{OH}^-], \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]}.$$

Electrical neutrality requires the total positive and negative charge concentrations to be equal:

$$[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-].$$

Substitution gives

$$[\text{H}^+] = c_{\text{HCl}} + \frac{K_w}{[\text{H}^+]},$$

which is **option (b)**.

Equivalently, setting $h = [\text{H}^+]$,

$$h^2 - c_{\text{HCl}}h - K_w = 0.$$

The physically admissible, positive root is

$$[\text{H}^+] = \frac{c_{\text{HCl}} + \sqrt{c_{\text{HCl}}^2 + 4K_w}}{2}.$$

With concentrations expressed in mol L^{-1} , the given concentration product is $K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$. As $c_{\text{HCl}} \rightarrow 0$, this expression correctly approaches

$$[\text{H}^+] \rightarrow \sqrt{K_w} = 1 \times 10^{-7} \text{ mol L}^{-1}.$$

Option (a) neglects water's contribution and is only an approximation when $c_{\text{HCl}} \gg \sqrt{K_w}$. Option (c) adds K_w instead of the hydroxide concentration; option (d) has the wrong sign in the charge balance. The stated exactness is within the problem's complete-dissociation, concentration-based equilibrium model.

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

Problem 3: Statements about a glucose solution

The molar mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 180 g mol^{-1} and N_A is the Avogadro constant. Which one of the following statements is not correct?

- (a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 cm^3 of solution. ()
- (b) 1.00 mmol amount of glucose has a mass of 180 mg. ()
- (c) 0.0100 mol of glucose comprises of $0.0100 \times 24 \times N_A$ atoms. ()
- (d) 90.0 g glucose contain $3 \times N_A$ atoms of carbon. ()
- (e) 100 cm^3 of a 0.10 M solution contain 18 g of glucose. ()

Official English text of the problem.

Answers

- (a) Correct.
- (b) Correct.
- (c) Correct.
- (d) Correct.

- **(e) Incorrect:** the solution contains **1.8 g** of glucose.

Solution

Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, has the open-chain connectivity SMILES O=CC(O)C(O)C(O)C(O)CO. Stereochemistry is omitted because it does not affect these calculations.

We use

$$n = \frac{m}{M}, \quad c = \frac{n}{V},$$

where $M = 180 \text{ g mol}^{-1}$ and V is the final solution volume in litres.

(a) The amount of glucose is

$$n = \frac{90 \text{ g}}{180 \text{ g mol}^{-1}} = 0.5 \text{ mol}.$$

Since $1000 \text{ cm}^3 = 1 \text{ L}$,

$$c = \frac{0.5 \text{ mol}}{1 \text{ L}} = 0.5 \text{ mol L}^{-1} = 0.5 \text{ M}.$$

The statement is correct.

(b) Converting millimoles to moles gives

$$m = nM = (1.00 \times 10^{-3} \text{ mol})(180 \text{ g mol}^{-1}) = 0.180 \text{ g} = 180 \text{ mg}.$$

The statement is correct.

(c) Each glucose molecule contains

$$6 + 12 + 6 = 24 \text{ atoms}.$$

The sample contains $0.0100N_A$ glucose molecules, so its total number of atoms is

$$N_{\text{atoms}} = 24 \times 0.0100N_A = 0.240N_A.$$

The statement is correct.

(d) The amount of glucose is

$$n = \frac{90.0 \text{ g}}{180 \text{ g mol}^{-1}} = 0.500 \text{ mol}.$$

Each glucose molecule contains six carbon atoms. Therefore, the sample contains

$$N_{\text{carbon atoms}} = 6 \times 0.500N_A = 3.00N_A.$$

The statement is correct.

(e) The solution volume is

$$100 \text{ cm}^3 = 0.100 \text{ L}.$$

Hence,

$$n = cV = (0.10 \text{ mol L}^{-1})(0.100 \text{ L}) = 0.010 \text{ mol},$$

and

$$m = nM = (0.010 \text{ mol})(180 \text{ g mol}^{-1}) = \boxed{1.8 \text{ g}}.$$

The stated mass of 18 g is ten times too large. Thus, **(e) is the single incorrect statement.**

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

Problem 4: Number of molecules in a liquid

If the density of a liquid compound B is ρ (in g cm^{-3}), M is the molar mass of B and N_A is the Avogadro constant, then the number of molecules of B in 1 dm^3 of this compound is:

(a) $(1000 \times \rho)/(M \times N_A)$ ()

(b) $(1000 \times \rho \times N_A)/M$ ()

(c) $(N_A \times \rho)/(M \times 1000)$ ()

(d) $(N_A \times \rho \times M)/1000$ ()

Official English text of the problem.

Answers

- 4. **(b)** $N = \frac{1000\rho N_A}{M}$ molecules. Mark the box beside **(b)**; leave the other boxes blank.

Solution

The volume is

$$V = 1 \text{ dm}^3 = 1000 \text{ cm}^3.$$

The mass of the liquid is $m = \rho V$, and its amount of substance is

$$n = \frac{m}{M} = \frac{\rho V}{M}.$$

Multiplying the amount of substance by the Avogadro constant gives the number of molecules:

$$N = nN_A = \frac{\rho V N_A}{M}.$$

With ρ expressed in g cm^{-3} , M in g mol^{-1} , and N_A in mol^{-1} , substitution yields

$$N = \frac{1000\rho N_A}{M}.$$

The units cancel as required for a count:

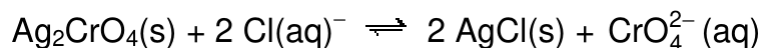
$$\frac{(\text{g cm}^{-3})(\text{cm}^3)}{\text{g mol}^{-1}} \text{mol}^{-1} = 1.$$

Therefore, **(b)** is correct.

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

Problem 5: Converting silver chromate into silver chloride

The equilibrium constant of the reaction:



is given by the equation:

(a) $K = K_{sp}(\text{Ag}_2\text{CrO}_4)/K_{sp}(\text{AgCl})^2$ ()

(b) $K = K_{sp}(\text{Ag}_2\text{CrO}_4) \times K_{sp}(\text{AgCl})^2$ ()

(c) $K = K_{sp}(\text{AgCl})/K_{sp}(\text{Ag}_2\text{CrO}_4)$ ()

(d) $K = K_{sp}(\text{AgCl})^2/K_{sp}(\text{Ag}_2\text{CrO}_4)$ ()

(e) $K = K_{sp}(\text{Ag}_2\text{CrO}_4)/K_{sp}(\text{AgCl})$ ()

Official English text of the problem.

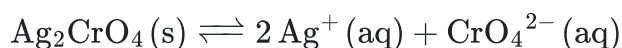
Answers

- **(a) Correct.** Tick this box: $K = \frac{K_{sp}(\text{Ag}_2\text{CrO}_4)}{[K_{sp}(\text{AgCl})]^2}$.
- **(b)** Incorrect; leave blank.
- **(c)** Incorrect; leave blank.
- **(d)** Incorrect; leave blank.
- **(e)** Incorrect; leave blank.

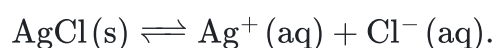
Solution

The species involved are silver chromate $[\text{Ag}^+] \cdot [\text{Ag}^+] \cdot [\text{O}^-][\text{Cr}](=\text{O})(=\text{O})[\text{O}^-]$, silver chloride $[\text{Ag}^+] \cdot [\text{Cl}^-]$, silver(I) ion $[\text{Ag}^+]$, chloride ion $[\text{Cl}^-]$, and chromate ion $[\text{O}^-][\text{Cr}](=\text{O})(=\text{O})[\text{O}^-]$. The salt SMILES specify their constituent ions and stoichiometry; the solids form extended ionic lattices. Chromate has tetrahedral coordination around chromium.

The two solubility equilibria are



and

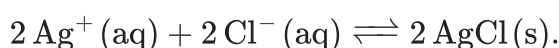


Using dimensionless activities and taking each pure solid's activity as unity,

$$K_{sp}(\text{Ag}_2\text{CrO}_4) = a(\text{Ag}^+)^2 a(\text{CrO}_4^{2-}),$$

$$K_{sp}(\text{AgCl}) = a(\text{Ag}^+) a(\text{Cl}^-).$$

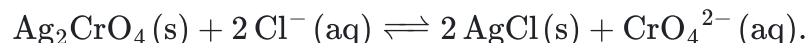
Reverse the second equilibrium and double it:



Reversing an equilibrium inverts its constant, and doubling its coefficients squares the constant. Thus this precipitation reaction has constant

$$\frac{1}{[K_{sp}(\text{AgCl})]^2}.$$

Adding it to silver chromate dissolution cancels the silver ions and gives the required reaction:



Equilibrium constants multiply when reactions are added, so

$$K = \frac{K_{sp}(\text{Ag}_2\text{CrO}_4)}{[K_{sp}(\text{AgCl})]^2}.$$

Equivalently, division of the solubility-product expressions gives

$$K = \frac{a(\text{CrO}_4^{2-})}{a(\text{Cl}^-)^2},$$

which is exactly the equilibrium expression for the stated reaction. Therefore **(a)** is the correct choice.

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

Problem 6: Preparing a phosphate buffer

How many cm^3 of 1.00 M NaOH solution must be added to 100.0 cm^3 of 0.100 M H_3PO_4 solution to obtain a phosphate buffer solution with pH of about 7.2? (The pK values for H_3PO_4 are $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

- (a) 5.0 cm^3 ()
- (b) 10.0 cm^3 ()
- (c) 15.0 mL ()
- (d) 20.0 mL ()

Official English text of the problem.

Answers

- **6. (c):** Add $15.0\text{ cm}^3 = 15.0\text{ mL}$ of 1.00 M sodium hydroxide solution.

Solution

6. The buffer pair associated with $pK_2 = 7.2$ is:

- Dihydrogen phosphate, H_2PO_4^- : $\text{O}=\text{P}(\text{O})(\text{O})[\text{O}^-]$.
- Hydrogen phosphate, HPO_4^{2-} : $\text{O}=\text{P}(\text{O})([\text{O}^-])[\text{O}^-]$.

The Henderson–Hasselbalch equation is

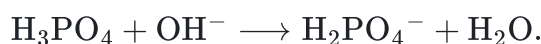
$$pH = pK_2 + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}.$$

Thus, $pH = pK_2 = 7.2$ requires equal concentrations, and therefore equal amounts, of these two ions. The widely separated pK_1 and pK_3 justify neglecting the other phosphate forms at this pH.

Initially, the amount of phosphoric acid, H_3PO_4 ($\text{O}=\text{P}(\text{O})(\text{O})\text{O}$), is

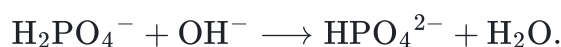
$$n_0 = (0.100 \text{ mol L}^{-1})(0.1000 \text{ L}) = 0.0100 \text{ mol}.$$

Sodium hydroxide ($[\text{Na}^+] \cdot [\text{OH}^-]$) supplies hydroxide ions, OH^- ($[\text{OH}^-]$). First, one equivalent neutralizes phosphoric acid to dihydrogen phosphate:



This consumes 0.0100 mol of hydroxide.

Next, half of the dihydrogen phosphate must be converted to hydrogen phosphate:



This consumes another

$$\frac{0.0100}{2} = 0.00500 \text{ mol}$$

of hydroxide, leaving 0.00500 mol of each buffer component.

In these equations, H_2O is water (O); the sodium ion, Na^+ ($[\text{Na}^+]$), is a spectator.

The total amount of sodium hydroxide required is therefore

$$n(\text{NaOH}) = 0.0100 + 0.00500 = 0.0150 \text{ mol},$$

giving

$$V = \frac{0.0150 \text{ mol}}{1.00 \text{ mol L}^{-1}} = 0.0150 \text{ L} = \boxed{15.0 \text{ cm}^3}.$$

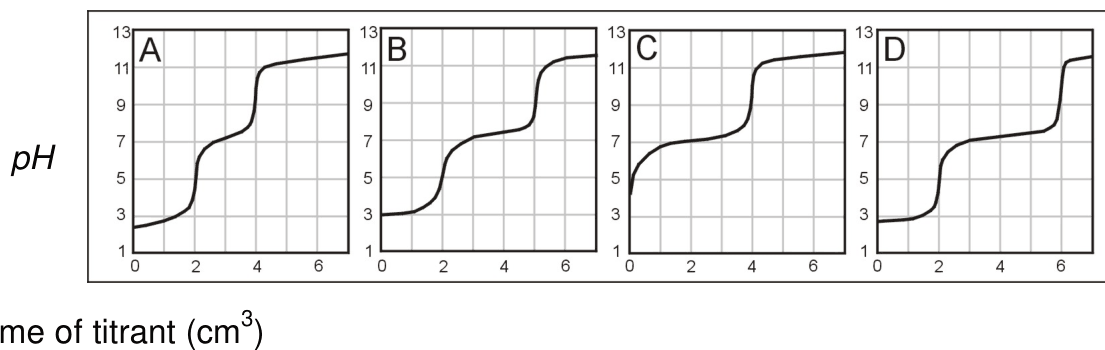
Hence, select **(c)**.

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

Problem 7: Titration curves of phosphate solutions

Solutions containing H_3PO_4 and/or NaH_2PO_4 are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (pH vs. volume of titrant) shown in the figure:

(For H_3PO_4 : $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)



a) The sample contains H_3PO_4 only.

Curve A (), Curve B (), Curve C (), Curve D ()

b) The sample contains both in a mole ratio $\text{H}_3\text{PO}_4 : \text{NaH}_2\text{PO}_4 = 2 : 1$.

Curve A (), Curve B (), Curve C (), Curve D ()

c) The sample contains both in a mole ratio $\text{H}_3\text{PO}_4 : \text{NaH}_2\text{PO}_4 = 1 : 1$.

Curve A (), Curve B (), Curve C (), Curve D ()

Official English text of the problem.

Answers

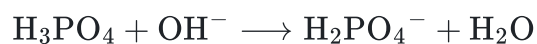
- a) Curve A.
- b) Curve B.
- c) Curve D.

Solution

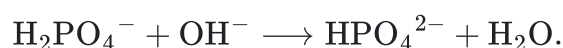
The chemical species needed for the explanation are:

Name	Formula	SMILES
Phosphoric acid	H_3PO_4	<chem>O=P(O)(O)O</chem>
Sodium dihydrogen phosphate	NaH_2PO_4	<chem>[Na+].O=P([O-])(O)O</chem>
Dihydrogen phosphate ion	H_2PO_4^-	<chem>O=P([O-])(O)O</chem>
Hydrogen phosphate ion	HPO_4^{2-}	<chem>O=P([O-])([O-])O</chem>
Hydroxide ion	OH^-	<chem>[OH-]</chem>
Water	H_2O	<chem>O</chem>

Let the initial amounts of phosphoric acid and sodium dihydrogen phosphate be a and b mol, respectively. The two observed equivalence points correspond to the successive neutralizations



and



Reaching the first equivalence point requires a mol of hydroxide. At that point, the solution contains $a + b$ mol of dihydrogen phosphate, so reaching the second equivalence point requires a further $a + b$ mol of hydroxide.

Thus, for base concentration c_B in mol L^{-1} and cumulative equivalence-point volumes V_1, V_2 in litres,

$$c_B V_1 = a, \quad c_B V_2 = 2a + b.$$

Consequently,

$$\boxed{\frac{V_2}{V_1} = 2 + \frac{b}{a}} \quad \text{and} \quad \boxed{a : b = V_1 : (V_2 - 2V_1)}.$$

The widely separated pK_i values allow these neutralization stages to be distinguished. The approximate pH values at the first and second equivalence points are, respectively,

$$\frac{pK_1 + pK_2}{2} = 4.65, \quad \frac{pK_2 + pK_3}{2} = 9.6,$$

consistent with the two steep rises shown.

a) Phosphoric acid only

Here $b = 0$, giving

$$V_2 = 2V_1.$$

Curve A has equivalence points at approximately 2 cm^3 and 4 cm^3 , so it satisfies this condition. **Mark Curve A.**

b) Mole ratio $\text{H}_3\text{PO}_4 : \text{NaH}_2\text{PO}_4 = 2 : 1$

Here $b/a = 1/2$, so

$$\frac{V_2}{V_1} = 2 + \frac{1}{2} = 2.5.$$

Curve B has equivalence points at approximately 2 cm^3 and 5 cm^3 . Equivalently,

$$a : b = 2 : (5 - 2 \times 2) = 2 : 1.$$

Mark Curve B.

c) Mole ratio $\text{H}_3\text{PO}_4 : \text{NaH}_2\text{PO}_4 = 1 : 1$

Here $b/a = 1$, so

$$\frac{V_2}{V_1} = 3.$$

Curve D has equivalence points at approximately 2 cm^3 and 6 cm^3 . Hence,

$$a : b = 2 : (6 - 2 \times 2) = 2 : 2 = 1 : 1.$$

Mark Curve D.

The remaining curve, **C**, corresponds to sodium dihydrogen phosphate alone. It begins near the amphiprotic dihydrogen phosphate pH, approximately 4.65, and has no initial phosphoric-acid neutralization step. Its prominent rise corresponds to conversion into hydrogen phosphate.

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

Problem 8: A dimethylhydrazine and dinitrogen tetroxide propellant

A fuel/oxidant system consisting of N,N-dimethylhydrazine $(\text{CH}_3)_2\text{NNH}_2$ and N_2O_4 (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N_2 , CO_2 and H_2O are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 1 mol of $(\text{CH}_3)_2\text{NNH}_2$?

- (a) 8 ()
- (b) 9 ()
- (c) 10 ()
- (d) 11 ()
- (e) 12 ()

Official English text of the problem.

Answers

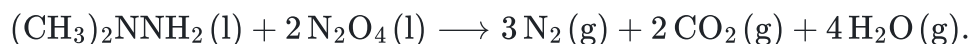
- 8. (b): of gases.

Solution

8. N,N-dimethylhydrazine $(\text{CN}(\text{C})\text{N})$ has molecular formula $\text{C}_2\text{H}_8\text{N}_2$. For 1 mol of fuel:

- Balancing carbon gives 2 mol of carbon dioxide, CO_2 ($\text{O}=\text{C}=\text{O}$).
- Balancing hydrogen gives 4 mol of water, H_2O (O).
- These products require $2(2) + 4 = 8$ mol of oxygen atoms, supplied by 2 mol of dinitrogen tetroxide, N_2O_4 ($[\text{O}-][\text{N}+](=\text{O})[\text{N}+](=\text{O})[\text{O}-]$).
- The reactants therefore contain $2 + 2(2) = 6$ mol of nitrogen atoms, producing 3 mol of dinitrogen, N_2 ($\text{N}\#\text{N}$).

The balanced reaction is



All three products are gases under the stated conditions, so

$$n_{\text{gas}} = (3 + 2 + 4) \text{ mol} = \text{9 mol}.$$

Thus, select (b).

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

Problem 9: Charge needed to electrolyse water

The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

- (a) F ()

(b) $(4/3) F$ ()

(c) $(3/2) F$ ()

(d) $2 F$ ()

(e) $3 F$ ()

Official English text of the problem.

Answers

- **9: (d) $2F$.** Mark the box for (d); leave the other boxes blank.

Solution

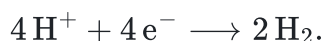
The overall electrolysis reaction is



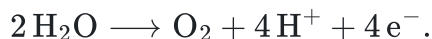
The molecular species are water (o), hydrogen ([H][H]), and oxygen (o=o).

Using acidic half-equations, with hydrogen ions H^+ ([H+]):

- At the cathode, reduction occurs:



- At the anode, oxidation occurs:



Adding these gives the overall reaction above. Thus, electrolysing 2 mol of water requires 4 mol of electrons to pass through the circuit. For 1 mol of water,

$$n(\text{e}^-) = 1 \text{ mol} \times \frac{4}{2} = 2 \text{ mol}.$$

By Faraday's law,

$$Q = n(\text{e}^-)F = (2 \text{ mol})F.$$

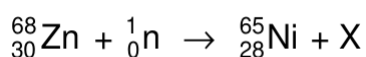
This is **two faradays of charge**, written $2F$ in the options, so **(d)** is correct. The electrode charges are not added: the same charge passes through both electrodes.

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

Problem 10: Particles emitted in nuclear reactions

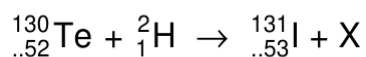
Identify particle X in each of the following nuclear reactions:

a)



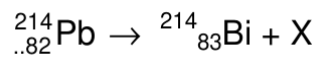
alpha (), beta (), gamma (), neutron ()

b)



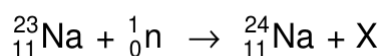
alpha (), beta (), gamma (), neutron ()

c)



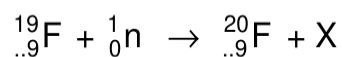
alpha (), beta (), gamma (), neutron ()

d)



alpha (), beta (), gamma (), neutron ()

e)



alpha (), beta (), gamma (), neutron ()

Official English text of the problem.

Answers

- **a)** Alpha particle, α : a helium-4 nucleus, ^4_2He , equivalent to the helium-4 dication $[^4\text{He}+2]$. Mark **alpha**.
- **b)** Neutron, ^1_0n . Mark **neutron**.
- **c)** Beta-minus particle, β^- : an electron, $^0_{-1}\text{e}$. Mark **beta**.
- **d)** Gamma photon, γ . Mark **gamma**.
- **e)** Gamma photon, γ . Mark **gamma**.

Solution

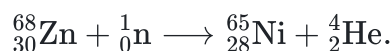
Nuclear equations conserve total mass number A and electric charge. Thus, the sums of the superscripts and of the subscripts must each be equal on both sides. For an emitted electron, the subscript is -1 , representing its charge in units of the elementary charge.

a)

The missing particle has

$$A_X = 68 + 1 - 65 = 4, \quad Z_X = 30 + 0 - 28 = 2.$$

These values identify a helium-4 nucleus, an **alpha particle**:

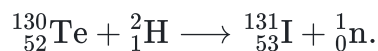


b)

The missing particle has

$$A_X = 130 + 2 - 131 = 1, \quad Z_X = 52 + 1 - 53 = 0.$$

A particle with mass number 1 and no electric charge is a **neutron**:

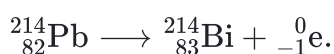


c)

The missing particle has

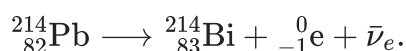
$$A_X = 214 - 214 = 0, \quad Z_X = 82 - 83 = -1.$$

It is an electron, corresponding to **beta-minus emission**:



The mass number remains unchanged while the nuclear charge increases by one: a neutron in the nucleus converts into a proton.

The equation above follows the problem's abbreviated notation. Physically, beta-minus decay also emits an electron antineutrino:



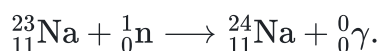
The antineutrino has zero electric charge and zero mass number, so it does not alter the identification of X as the beta particle.

d)

The missing particle has

$$A_X = 23 + 1 - 24 = 0, \quad Z_X = 11 + 0 - 11 = 0.$$

Among the listed choices, this identifies a **gamma photon**. Neutron capture produces an excited sodium-24 nucleus, which releases excitation energy as gamma radiation:

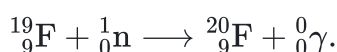


e)

The missing particle has

$$A_X = 19 + 1 - 20 = 0, \quad Z_X = 9 + 0 - 9 = 0.$$

Again, the appropriate listed particle is a **gamma photon**, emitted as the fluorine-20 nucleus releases excitation energy following neutron capture:



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

Problem 11: Heat of neutralisation in a calorimeter

10.0 cm³ of 0.50 M HCl and 10.0 cm³ of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of ΔT is recorded. Estimate the temperature increase if 5.0 cm³ of 0.50 M NaOH were used instead of 10.0 cm³. Thermal losses are negligible and the specific heats of both solutions are taken as equal.

(a) $(1/2) \Delta T$ ()

(b) $(2/3) \Delta T$ ()

(c) $(3/4) \Delta T$ ()

(d) ΔT ()

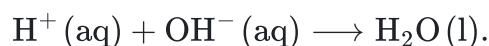
Official English text of the problem.

Answers

- 11: (b) $\Delta T_{\text{new}} = \frac{2}{3} \Delta T$. Mark the parentheses beside (b).

Solution

11. The net neutralisation reaction is



The species are hydrogen ion [H⁺], hydroxide ion [OH⁻], and water.

In the original experiment, the amounts of acid and base are each

$$n_1 = (0.50 \text{ mol L}^{-1})(10.0 \times 10^{-3} \text{ L}) = 5.0 \times 10^{-3} \text{ mol}.$$

They react completely in a 1 : 1 ratio. With only 5.0 cm³ of base, hydroxide becomes the limiting reactant:

$$n_2 = (0.50 \text{ mol L}^{-1})(5.0 \times 10^{-3} \text{ L}) = 2.5 \times 10^{-3} \text{ mol}.$$

The amount neutralised is halved, so the heat released is halved:

$$\frac{q_2}{q_1} = \frac{n_2}{n_1} = \frac{1}{2}.$$

For the estimate, take the dilute solutions to have equal densities. The ratio of their total masses is then

$$\frac{m_2}{m_1} = \frac{10.0 + 5.0}{10.0 + 10.0} = \frac{3}{4}.$$

Neglecting the calorimeter's heat capacity, $q = mc\Delta T$. Since the specific heat capacity c is the same in both experiments,

$$\frac{\Delta T_{\text{new}}}{\Delta T} = \frac{q_2}{q_1} \frac{m_1}{m_2} = \frac{1}{2} \times \frac{4}{3} = \frac{2}{3}.$$

Thus the correct choice is **(b)**.

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

Problem 12: Mass spectrum of the SbHCl⁺ ion

Natural antimony consists of the following 2 stable isotopes: ^{121}Sb , ^{123}Sb . Natural chlorine consists of the following 2 stable isotopes: ^{35}Cl , ^{37}Cl . Natural hydrogen consists of the following 2 stable isotopes: ^1H , ^2H . How many peaks are expected in a low resolution mass spectrum for the ionic fragment SbHCl^+ ?

- (a) 4 (☐)
- (b) 5 (☐)
- (c) 6 (☐)
- (d) 7 (☐)
- (e) 8 (☐)
- (f) 9 (☐)

Official English text of the problem.

Answers

- **12. (c) 6 peaks**, at nominal $m/z = 157, 158, 159, 160, 161, 162$.

Solution

12. The fragment is the chloridohydridoantimony(1+) ion, SbHCl^+ , represented by SMILES [H][Sb+][Cl].

Each element has two isotopes, giving

$$2 \times 2 \times 2 = 8$$

possible isotopic combinations. In a low resolution mass spectrum, combinations with the same **nominal mass** contribute to the same peak.

For this singly charged ion, the nominal m/z is obtained by adding the three isotope mass numbers. The eight combinations give:

Antimony isotope	Chlorine isotope	Nominal m/z with ^1H	Nominal m/z with ^2H
^{121}Sb	^{35}Cl	157	158
^{121}Sb	^{37}Cl	159	160
^{123}Sb	^{35}Cl	159	160
^{123}Sb	^{37}Cl	161	162

The tabulated mass-to-charge ratios are in Th, where $1 \text{ Th} = 1 \text{ u/e}$.

Replacing ^{121}Sb with ^{123}Sb or replacing ^{35}Cl with ^{37}Cl increases the nominal mass by the same amount, 2 u. Consequently, two combinations overlap at 159 and another two overlap at 160. Their small exact-mass differences are unresolved at low resolution.

Thus there are **six distinct peaks**, so the correct choice is **(c)**. Isotope abundances determine their relative intensities.

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

Problem 13: X-ray diffraction angles

The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5° . Based on this we must expect a beam of X-rays diffracted at:

- (a) 22.0 degrees (☐)
- (b) 22.5 degrees (☐)
- (c) 23.0 degrees (☐)
- (d) 23.5 degrees (☐)
- (e) 24.0 degrees (☐)
- (f) 24.5 degrees (☐)

Official English text of the problem.

Answers

- (a) Incorrect.
- (b) Incorrect.
- (c) Incorrect.
- **(d) Correct: 23.5° .**
- (e) Incorrect.
- (f) Incorrect.

Solution

Constructive interference of X-rays reflected from successive crystal planes obeys **Bragg's law**:

$$2d \sin \theta_n = n\lambda,$$

where d is the spacing between the planes, λ is the X-ray wavelength, and $n = 1, 2, \dots$ is the diffraction order. Here θ_n is the Bragg angle, measured relative to the planes.

The smallest diffraction angle corresponds to the first order, $n = 1$:

$$2d \sin 11.5^\circ = \lambda.$$

For the second order,

$$2d \sin \theta_2 = 2\lambda.$$

Dividing these equations eliminates both d and λ :

$$\sin \theta_2 = 2 \sin 11.5^\circ = 0.3987359.$$

Therefore,

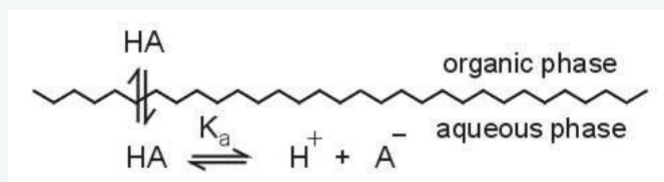
$$\theta_2 = \arcsin(0.3987359) = 23.4992^\circ \approx \boxed{23.5^\circ}.$$

Thus **(d)** is the correct choice. The other listed angles do not correspond to an integer diffraction order. On the answer sheet, mark **(d)** and leave **(a)**, **(b)**, **(c)**, **(e)**, and **(f)** unmarked.

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

Problem 14: Extraction of a weak acid

The undissociated form of a weak organic acid **HA** can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:



Regarding this extraction, are the following statements correct (Y) or not (N)?

- (a) The distribution constant (K_D) of the acid **HA** depends on the pH of the aqueous phase. (Y) (N)
- (b) **HA** can be efficiently extracted only from acidic aqueous solutions. (Y) (N)
- (c) The distribution ratio (D) of the acid **HA** depends on the pH of the aqueous phase. (Y) (N)
- (d) The distribution ratio (D) of the acid **HA** depends mainly on its concentration. (Y) (N)

Official English text of the problem.

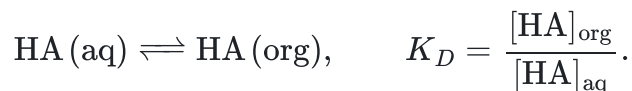
Answers

- **(a)** N
- **(b)** Y, under the intended qualitative interpretation.
- **(c)** Y
- **(d)** N

Solution

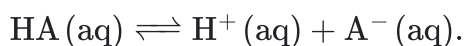
The symbols **HA** and **A⁻** denote an unspecified weak organic acid and its conjugate-base ion. Their molecular structures are not given, so unique names and SMILES cannot be assigned. The hydrogen ion **H⁺** is a proton, [H+].

(a) The distribution constant refers to the **same chemical species**, undissociated **HA**, in the two phases:



For the stated model, at fixed temperature and solvent composition, K_D is independent of aqueous pH. Changing pH changes how much acid is undissociated, but does not change this partition constant. Hence **N**.

(b) In the aqueous phase, the acid dissociates:



Using the dilute-solution approximation,

$$K_a = \frac{[\text{H}^+]_{\text{aq}}[\text{A}^-]_{\text{aq}}}{[\text{HA}]_{\text{aq}}},$$

and therefore

$$\frac{[\text{A}^-]_{\text{aq}}}{[\text{HA}]_{\text{aq}}} = \frac{K_a}{[\text{H}^+]_{\text{aq}}} = 10^{\text{pH} - \text{p}K_a}.$$

The fraction of aqueous acid present in its extractable, undissociated form is thus

$$\alpha_{\text{HA}} = \frac{1}{1 + 10^{\text{pH} - \text{p}K_a}}.$$

Acidification suppresses dissociation. When $\text{pH} \ll \text{p}K_a$, almost all the aqueous acid is undissociated and available for extraction. Increasing pH favors the conjugate-base ion, which remains in the aqueous phase in the given scheme. This supports the intended qualitative answer **Y**.

(c) The distribution ratio uses the **total analytical concentration of the acid** in each phase. Since only undissociated acid enters the organic phase,

$$D = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}}.$$

Substituting the partition and dissociation relations gives

$$D = \frac{K_D [\text{HA}]_{\text{aq}}}{[\text{HA}]_{\text{aq}} (1 + K_a / [\text{H}^+]_{\text{aq}})} = \boxed{\frac{K_D}{1 + 10^{\text{pH} - \text{p}K_a}}}.$$

Thus D depends on pH and decreases as pH increases. Hence **Y**.

(d) The expression above contains no total acid concentration. At fixed pH, temperature, and solvent composition, D is independent of the acid's analytical concentration within the stated model. Hence **N**.

In an unbuffered solution, changing the acid concentration can change pH and thereby affect D indirectly; this does not make concentration its principal independent determinant.

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

Problem 15: Statements about Beer's law

Regarding Beer's law, are the following statements correct (Y) or not (N)?

(a) The absorbance is proportional to the concentration of the absorbing compound. (Y) (N)

- (b) The absorbance is linearly related to the wavelength of the incident light. (Y) (N)
- (c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. (Y) (N)
- (d) The transmittance is inversely proportional to the logarithm of absorbance. (Y) (N)
- (e) The transmittance is inversely proportional to the concentration of the absorbing compound. (Y) (N)

Official English text of the problem.

Answers

- (a) Y
- (b) N
- (c) Y
- (d) N
- (e) N

Solution

The Beer–Lambert law is

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \varepsilon(\lambda) \ell c,$$

where I_0 and I are the incident and transmitted light intensities, $\varepsilon(\lambda)$ is the molar absorption coefficient at wavelength λ , ℓ is the optical path length, and c is the concentration.

Transmittance is defined as $T = I/I_0$, so

$$A = -\log_{10} T, \quad T = 10^{-A} = 10^{-\varepsilon(\lambda) \ell c}.$$

Both A and T are dimensionless. For example, with ℓ in cm and c in mol L^{-1} , ε has units of $\text{L mol}^{-1} \text{cm}^{-1}$.

(a) Correct (Y). At fixed wavelength and optical path length, within the conditions where Beer's law applies,

$$A = [\varepsilon(\lambda) \ell] c.$$

Thus absorbance is proportional to concentration.

(b) Incorrect (N). The wavelength dependence of absorbance comes through $\varepsilon(\lambda)$, which varies according to the absorption spectrum. Beer's law does not imply a linear relationship between absorbance and wavelength.

(c) Correct (Y). Rearranging the law gives

$$\log_{10} T = -\varepsilon(\lambda) \ell c.$$

Thus the logarithm of transmittance is proportional to concentration, with a negative proportionality constant. Choosing another logarithm base only changes that constant.

(d) Incorrect (N). The actual relationship is

$$T = 10^{-A},$$

rather than $T \propto 1/\log A$.

(e) Incorrect (N). At fixed wavelength and optical path length,

$$T = 10^{-\varepsilon(\lambda)\ell c}.$$

Transmittance decreases exponentially with concentration; it is not inversely proportional to concentration.

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

Problem 16: Wavelengths of monochromatic radiation

Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics:

a)	3000 Å	150 nm (), 300 nm (), 600 nm (), 5000 nm ()
b)	5×10^{14} Hz	150 nm (), 300 nm (), 600 nm (), 5000 nm ()
c)	2000 cm ⁻¹	150 nm (), 300 nm (), 600 nm (), 5000 nm ()
d)	2×10^6 GHz	150 nm (), 300 nm (), 600 nm (), 5000 nm ()

Official English text of the problem.

Answers

- **a)** 300 nm
- **b)** 600 nm
- **c)** 5000 nm
- **d)** 150 nm

Solution

Use the speed of light in vacuum, $c \approx 3.00 \times 10^8 \text{ m s}^{-1}$, and the relationships

$$\lambda = \frac{c}{\nu}, \quad \lambda = \frac{1}{\tilde{\nu}},$$

where ν is frequency and $\tilde{\nu}$ is wavenumber.

a) Since $1 \text{ Å} = 10^{-10} \text{ m} = 0.1 \text{ nm}$,

$$\lambda = 3000 \text{ Å} \times \frac{0.1 \text{ nm}}{1 \text{ Å}} = \boxed{300 \text{ nm}}.$$

b) Since $\text{Hz} = \text{s}^{-1}$,

$$\lambda = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{5 \times 10^{14} \text{ s}^{-1}} = 6 \times 10^{-7} \text{ m} = \boxed{600 \text{ nm}}.$$

c) The quantity in cm^{-1} is the wavenumber. Taking its reciprocal gives the wavelength in centimetres:

$$\lambda = \frac{1}{2000 \text{ cm}^{-1}} = 5 \times 10^{-4} \text{ cm}.$$

Using $1 \text{ cm} = 10^7 \text{ nm}$,

$$\lambda = 5 \times 10^{-4} \text{ cm} \times \frac{10^7 \text{ nm}}{1 \text{ cm}} = \boxed{5000 \text{ nm}}.$$

d) First convert gigahertz to hertz:

$$\nu = 2 \times 10^6 \text{ GHz} \times \frac{10^9 \text{ Hz}}{1 \text{ GHz}} = 2 \times 10^{15} \text{ Hz}.$$

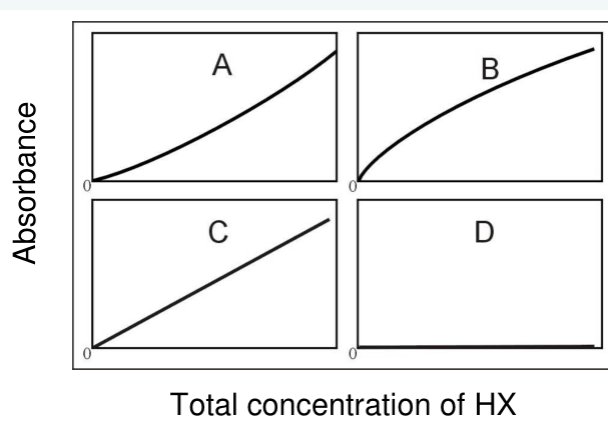
Therefore,

$$\lambda = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{2 \times 10^{15} \text{ s}^{-1}} = 1.5 \times 10^{-7} \text{ m} = \boxed{150 \text{ nm}}.$$

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

Problem 17: Working curves for a weak acid

The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:



a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb.

Curve A (), Curve B (), Curve C (), Curve D ()

b) Pure aqueous solutions of HX were used. Only the anionic species X^- absorb.

Curve A (), Curve B (), Curve C (), Curve D ()

c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb.

Curve A (), Curve B (), Curve C (), Curve D ()

d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb.

Curve A (), Curve B (), Curve C (), Curve D ()

e) Pure aqueous solutions of HX were used. Both HX and X^- absorb. Measurements were obtained at a wavelength where the molar absorptivities of X^- and HX are equal and different than zero.

Curve A (), Curve B (), Curve C (), Curve D ()

Official English text of the problem.

Answers

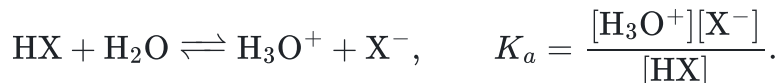
- **a)** Curve **A** — increasing, concave upward.
- **b)** Curve **B** — increasing, concave downward.
- **c)** Curve **D** — essentially zero absorbance.
- **d)** Curve **C** — straight line through the origin.
- **e)** Curve **C** — straight line through the origin.

Solution

Let the total analytical concentration be

$$c = [\text{HX}] + [\text{X}^-].$$

The acid dissociation equilibrium is



Here, HX is an unspecified monoprotic weak acid and X^- its conjugate base; their structures are not given, so unique molecular SMILES cannot be assigned. The other species used are water H_2O , O ; hydronium H_3O^+ , $[\text{OH}_3^+]$; and hydroxide OH^- , $[\text{OH}^-]$.

At a fixed wavelength and optical path length ℓ , the Beer–Lambert law gives the absorbance $\mathcal{A}$:

$$\mathcal{A} = \ell (\varepsilon_{\text{HX}}[\text{HX}] + \varepsilon_{\text{X}^-}[\text{X}^-]).$$

With concentrations in mol L^{-1} , ℓ in cm , and molar absorptivities in $\text{L mol}^{-1} \text{cm}^{-1}$, absorbance is dimensionless.

a) In pure aqueous acid solutions, neglecting water's contribution to the hydronium concentration, put

$$x = [\text{X}^-] = [\text{H}_3\text{O}^+], \quad [\text{HX}] = c - x.$$

Then

$$K_a = \frac{x^2}{c - x}, \quad x = \frac{\sqrt{K_a^2 + 4K_a c} - K_a}{2}.$$

This function increases with c but is concave downward:

$$\frac{d^2 x}{dc^2} = -\frac{2K_a^2}{(K_a^2 + 4K_a c)^{3/2}} < 0.$$

Consequently, $c - x = [\text{HX}]$ is concave upward. Since only undissociated acid absorbs,

$$\mathcal{A} = \varepsilon_{\text{HX}} \ell (c - x).$$

The absorbance therefore increases with an increasing slope: **curve A**. Chemically, increasing the acid concentration decreases its fraction dissociated, so the fraction present as absorbing HX increases.

b) Only the conjugate base absorbs:

$$\mathcal{A} = \varepsilon_{\text{X}^-} \ell x.$$

The expression for x above is increasing and concave downward. Although the absolute concentration of X^- increases, its fraction of the total acid decreases as c increases. Thus the absorbance rises with a decreasing slope: **curve B**.

c) Excess strong base converts the acid essentially completely into its conjugate base:



Under the intended complete-neutralization approximation,

$$[\text{HX}] \approx 0.$$

Because only HX absorbs,

$$\mathcal{A} = \varepsilon_{\text{HX}} \ell [\text{HX}] \approx 0.$$

The working curve lies along the horizontal concentration axis: **curve D**.

d) Excess strong acid suppresses dissociation of the weak acid:

$$\frac{[\text{X}^-]}{[\text{HX}]} = \frac{K_a}{[\text{H}_3\text{O}^+]} \ll 1.$$

Hence essentially all the analytical acid remains undissociated:

$$[\text{HX}] \approx c, \quad \mathcal{A} \approx \varepsilon_{\text{HX}} \ell c.$$

The absorbance is proportional to total concentration, giving a straight line through the origin: **curve C**.

e) Let the equal, nonzero molar absorptivities be

$$\varepsilon_{\text{HX}} = \varepsilon_{\text{X}^-} = \varepsilon > 0.$$

The absorbances of the two species add:

$$\begin{aligned} \mathcal{A} &= \varepsilon \ell [\text{HX}] + \varepsilon \ell [\text{X}^-] \\ &= \varepsilon \ell ([\text{HX}] + [\text{X}^-]) \\ &= \varepsilon \ell c. \end{aligned}$$

Thus dissociation does not affect the absorbance at this wavelength. The working curve is a straight line through the origin: **curve C**.

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

Problem 18: The strongest chlorine oxoacid

Which of the following acids is the strongest?

a) perchloric acid, HClO_4 ()

b) chloric acid, HClO_3 ()

- c) chlorous acid, HClO_2 ()
- d) hypochlorous, HClO ()
- (e) All of them are equally strong because they all contain chlorine ()

Official English text of the problem.

Answers

- **18: a)** Perchloric acid, HClO_4 , SMILES OC1(=O)(=O)=O. Mark only the box beside **a**).

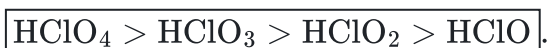
Solution

18. The four acids have the following structures, written using conventional localized bonds:

Acid	SMILES
Perchloric acid	<chem>OC1(=O)(=O)=O</chem>
Chloric acid	<chem>OC1(=O)=O</chem>
Chlorous acid	<chem>OC1=O</chem>
Hypochlorous acid	<chem>OC1</chem>

For oxoacids of the same central element, acidity increases with the number of additional oxygen atoms attached to that element. These oxygen atoms withdraw electron density, stabilizing the conjugate base formed when the acidic $\text{O}-\text{H}$ group loses its proton. Delocalization of the conjugate base's negative charge over oxygen atoms also contributes to this stabilization.

Consequently, the acid-strength order is



Perchloric acid produces the particularly stable, weakly basic **perchlorate ion**, ClO_4^- , SMILES [O-]C1(=O)(=O)=O. This SMILES depicts one localized resonance form; the actual ion has equivalent chlorine–oxygen bonds, with its negative charge delocalized over all four oxygen atoms.

Thus **a) perchloric acid** is the strongest. Merely containing the same central element does not make these acids equally strong.

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

Problem 19: Crystal structure of iron

Which structure describes best the crystal system of iron in which the coordination number is 8?

- a) simple cubic ()
- b) body-centered cubic ()
- c) cubic closest packed ()
- d) hexagonal closest packed ()
- e) none of the above ()

Answers

- 19. b) body-centered cubic.

Solution

19. The coordination number is the number of nearest-neighbor atoms surrounding an atom.

In a **body-centered cubic (BCC)** structure, the atom at the center of a cubic unit cell has eight nearest neighbors, one at each corner. If the cube edge length is a , all eight neighbors lie at the same distance:

$$d = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{\sqrt{3}}{2}a.$$

Every atom has this equivalent environment, so the coordination number is **8**.

For comparison, simple cubic has coordination number 6, while cubic closest packed and hexagonal closest packed both have coordination number 12. Therefore, mark **b**).

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

Problem 20: Largest third ionisation energy

Which of the following elements has the largest third ionization energy?

- a) B ☐
- b) C ☐
- c) N ☐
- d) Mg ☐
- e) Al ☐

Official English text of the problem.

Answers

- 20. d) Mg, magnesium. Mark the box beside d).

Solution

20. The third ionization energy is the energy required to remove an electron from a gaseous doubly charged positive ion. Thus, compare the electron configurations **after the first two ionizations**:

Ion (name and SMILES)	Electron configuration	Electron removed in the third ionization
Boron dication, [B+2]	$1s^2 2s^1$	$2s$ valence electron
Carbon dication, [C+2]	$1s^2 2s^2$	$2s$ valence electron
Nitrogen dication, [N+2]	$1s^2 2s^2 2p^1$	$2p$ valence electron
Magnesium dication, [Mg+2]	$1s^2 2s^2 2p^6$	$2p$ core electron
Aluminium dication, [Al+2]	$1s^2 2s^2 2p^6 3s^1$	$3s$ valence electron

Magnesium has already lost both of its $3s$ valence electrons, leaving a closed shell with the electron configuration of neon. Its third ionization,



therefore removes an electron from this inner closed shell. The product is the magnesium trication, [Mg+3].

This core electron is strongly bound: it occupies the $n = 2$ shell and experiences the attraction of magnesium's nucleus with 12 protons. The $n = 2$ electrons removed from boron, carbon, and nitrogen are valence electrons in atoms with much lower nuclear charges. Aluminium instead loses its remaining $3s$ valence electron.

Consequently, **magnesium has the largest third ionization energy**.

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

Problem 21: A second-period element from its ionisation energies

Which second period (row) element has the first six ionization energies (IE in electron volts, eV) listed below?

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

- a) B ()
- b) C ()
- c) N ()
- d) O ()
- e) F ()

Official English text of the problem.

Answers

21. **b) Carbon, C**. Mark the box beside option b).

Solution

21. The decisive feature is the large increase between the fourth and fifth ionization energies:

$$IE_4 = 64 \text{ eV}, \quad IE_5 = 392 \text{ eV}.$$

This jump indicates that removing the first four electrons exhausts the outer shell. The fifth electron must then be removed from an inner shell, where electrons are much more strongly bound to the nucleus. Thus, the element has **four valence electrons**.

The second-period element with four valence electrons is carbon, whose ground-state electron configuration is

$$1s^2 2s^2 2p^2.$$

The first four ionizations remove the two $2p$ and two $2s$ electrons. The fifth and sixth remove the two inner-shell $1s$ electrons, accounting for their much higher ionization energies.

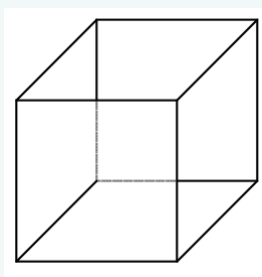
Therefore, the correct choice is **b) C**.

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

Problem 22: Face-centred cubic silver

Silver metal exists as a face-centered cubic (fcc) packed solid.

a) Draw an fcc unit cell.



b) How many atoms are present in the fcc unit cell?

c) The density of silver has been determined to be 10.5 g cm^{-3} . What is the length of each edge of the unit cell?

d) What is the atomic radius of the silver atoms in the crystal?

Official English text of the problem.

Answers

- **a)** A cube with atoms centered at all eight corners and at the centers of all six faces.
- **b)** 4 atoms per unit cell.
- **c)** $a = 4.09 \times 10^{-8} \text{ cm} = 409 \text{ pm}$.
- **d)** $r = 1.44 \times 10^{-8} \text{ cm} = 144 \text{ pm}$.

Solution

a) Draw a cube and place an atom at each of its eight vertices and at the center of each of its six faces, including the hidden faces. There is no atom at the body center. Neighboring atoms touch along the face diagonals.

b) Each corner atom is shared by eight unit cells, so it contributes $1/8$ atom to the cell. Each face-centered atom is shared by two cells, contributing $1/2$ atom. Therefore,

$$Z = 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = \boxed{4 \text{ atoms per unit cell}}.$$

c) Use the standard molar mass $M(\text{Ag}) = 107.87 \text{ g mol}^{-1}$ and Avogadro constant $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$.

The mass of one unit cell is

$$m_{\text{cell}} = \frac{ZM}{N_A} = \frac{4(107.87 \text{ g mol}^{-1})}{6.02214076 \times 10^{23} \text{ mol}^{-1}} = 7.16489 \times 10^{-22} \text{ g}.$$

For a cube of edge length a , the volume is a^3 . Hence,

$$\rho = \frac{m_{\text{cell}}}{a^3}, \quad a = \left(\frac{ZM}{\rho N_A} \right)^{1/3}.$$

Substituting,

$$a = \left[\frac{4(107.87)}{(10.5)(6.02214076 \times 10^{23})} \text{ cm}^3 \right]^{1/3} = 4.08639 \times 10^{-8} \text{ cm}.$$

To three significant figures,

$$\boxed{a = 4.09 \times 10^{-8} \text{ cm} = 0.409 \text{ nm} = 409 \text{ pm}}.$$

d) Along a face diagonal, a corner atom touches the face-centered atom, which touches the opposite corner atom. The two center-to-center distances are each $2r$, so the diagonal has length $4r$.

Geometrically, the face diagonal is $a\sqrt{2}$. Thus,

$$4r = a\sqrt{2}, \quad r = \frac{a}{2\sqrt{2}}.$$

Using the unrounded edge length,

$$r = \frac{408.639 \text{ pm}}{2\sqrt{2}} = 144.476 \text{ pm}.$$

To three significant figures,

$$\boxed{r = 144 \text{ pm} = 0.144 \text{ nm} = 1.44 \times 10^{-8} \text{ cm}}.$$

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

Problem 23: Hydrogen halides, buffers and electrolysis

Are the following statements correct (Y) or not (N)?

- a) HF boils at a higher temperature than HCl. (Y) (N)
- b) HBr boils at a lower temperature than HI (Y) (N)
- c) Pure HI can be produced by reacting concentrated sulfuric acid with KI. (Y) (N)
- d) Ammonia solutions are buffer solutions because they contain the conjugate pair $\text{NH}_3 - \text{NH}_4^+$. (Y) (N)
- e) Pure water at 80 °C is acidic. (Y) (N)
- f) During electrolysis of an aqueous KI solution with graphite electrodes, the pH near the cathode is below 7. (Y) (N)

Official English text of the problem.

Answers

- a) Y
- b) Y
- c) N
- d) N
- e) N
- f) N

Solution

a) Y — hydrogen bonding raises the boiling point of hydrogen fluoride.

Hydrogen fluoride, HF ($[\text{H}]\text{F}$), forms strong intermolecular hydrogen bonds. Hydrogen chloride, HCl ($[\text{H}]\text{Cl}$), has dipole–dipole and London dispersion attractions but lacks comparably strong hydrogen bonding.

Consequently, separating the molecules into the gas phase requires more energy for HF, giving it the higher boiling point despite its lower molar mass.

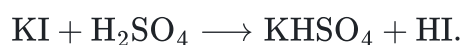
b) Y — dispersion forces are stronger in hydrogen iodide.

Hydrogen iodide, HI ($[\text{H}]\text{I}$), has a larger, more polarizable electron cloud than hydrogen bromide, HBr ($[\text{H}]\text{Br}$). Its stronger London dispersion forces produce a higher boiling point:

$$T_b(\text{HBr}) < T_b(\text{HI}).$$

c) N — concentrated sulfuric acid oxidizes hydrogen iodide.

An initial acid–base reaction between potassium iodide, KI ($[\text{K}^+] \cdot [\text{I}^-]$), and sulfuric acid, H_2SO_4 ($\text{OS}(=\text{O})(=\text{O})\text{O}$), can be written as



Here, KHSO_4 is potassium hydrogen sulfate ($[\text{K}^+] \cdot \text{OS}(=\text{O})(=\text{O})[\text{O}^-]$).

However, concentrated sulfuric acid also acts as an oxidizing agent. It oxidizes hydrogen iodide to iodine, I_2 (II). One possible subsequent redox reaction is

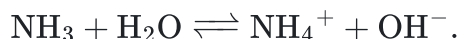


The other products in this equation are hydrogen sulfide, H_2S (s), and water, H_2O (o). Iodine changes oxidation state from -1 to 0 , while sulfur changes from $+6$ to -2 .

Thus, the reaction does not provide pure hydrogen iodide.

d) N — the presence of a conjugate pair alone is insufficient.

Ammonia, NH_3 (N), reacts weakly with water to form ammonium ions, NH_4^+ ($[\text{NH}_4^+]$), and hydroxide ions, OH^- ($[\text{OH}^-]$):

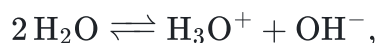


A useful buffer requires appreciable concentrations of both members of the conjugate pair, enabling it to consume added acid and added base without a large change in pH.

In an ordinary ammonia solution, only a small fraction of the ammonia forms ammonium ions. Their mere presence does not establish an effective buffer. An ammonia solution containing a suitable amount of an ammonium salt can form a buffer.

e) N — pure water remains neutral at 80 °C.

Water undergoes self-ionization:



where H_3O^+ is the hydronium ion ($[\text{OH}_3^+]$).

In pure water, the two ions are produced in equal amounts:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-].$$

This equality establishes neutrality. At 80 °C, the ionic product of water is greater than at 25 °C, so the neutral pH is below 7:

$$\text{pH}_{\text{neutral}} = \frac{1}{2} \text{p}K_{\text{w}}(80^\circ\text{C}) < 7.$$

A pH below 7 therefore does not make pure water acidic at this temperature.

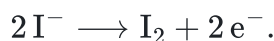
f) N — hydroxide is produced at the cathode.

In aqueous potassium iodide, water is reduced at the graphite cathode:

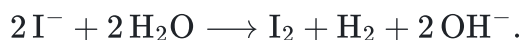


The gas produced is hydrogen, H_2 ($[\text{H}][\text{H}]$). Hydroxide accumulates near the cathode, making that region alkaline; under ordinary room-temperature conditions, its pH is above 7.

At the anode, iodide ions, I^- ($[\text{I}^-]$), are oxidized:



The corresponding overall electrode reaction is



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

Problem 24: Zinc and nitric acid

Under certain conditions of concentration and temperature HNO_3 reacts with Zn and its reduction products are NO_2 and NO in a molar ratio 1 : 3. How many moles of HNO_3 are consumed by 1 mol of Zn ?

- a) 2.2 ()
- b) 2.4 ()
- c) 2.6 ()
- d) 2.8 ()
- e) 3.0 ()
- f) 3.2 ()

Official English text of the problem.

Answers

- **24. d)** 2.8 mol of nitric acid, HNO_3 ($\text{O}=[\text{N}+](\text{O}-)\text{O}$), is consumed by 1 mol of zinc. Mark option **d)**.

Solution

24. Zinc is oxidized from oxidation state 0 to +2, so 1 mol of zinc releases 2 mol of electrons.

Nitrogen has oxidation state +5 in nitric acid. Its reduction products are:

- Nitrogen dioxide, NO_2 ($\text{O}=[\text{N}+](\text{O}-)$): nitrogen is +4, requiring **one electron** per molecule. This SMILES represents a radical using one formal charge arrangement.
- Nitrogen monoxide, NO ($[\text{N}]=\text{O}$): nitrogen is +2, requiring **three electrons** per molecule.

Let x mol of NO_2 and $3x$ mol of NO form per mole of zinc. Electron balance gives

$$x + 3(3x) = 2, \quad x = 0.20.$$

Thus, the amount of nitric acid **reduced** is

$$n_{\text{reduced}} = (0.20 + 0.60) \text{ mol} = 0.80 \text{ mol}.$$

Another 2 mol of nitric acid supplies the nitrate ions, NO_3^- ($[\text{O}-][\text{N}+](=\text{O})[\text{O}-]$), needed to form 1 mol of zinc(II) nitrate, $\text{Zn}(\text{NO}_3)_2$ ($[\text{Zn}+2] \cdot [\text{O}-][\text{N}+](=\text{O})[\text{O}-] \cdot [\text{O}-][\text{N}+](=\text{O})[\text{O}-]$). The salt's SMILES specifies its ionic composition.

The balanced overall reaction is



where H_2O is water (o).

Therefore,

$$n(\text{HNO}_3) = 2.00 + 0.80 = \span style="border: 1px solid black; padding: 2px;">2.8 \text{ mol}$$

per 1 mol of zinc, confirming **option d)**.

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

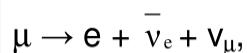
Problem 25: Muon

SECTION B: PHYSICAL CHEMISTRY

PROBLEM 25 Muon

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

a) The most common spontaneous disintegration reaction for the muon is:



where $\bar{\nu}_e$ is the electron antineutrino, and ν_μ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + \nu_\mu$, carried away a total energy of 2.000×10^{-12} J, while the electron was moving with a kinetic energy of 1.4846×10^{-11} J. Determine the mass of the muon.

b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a ^1H nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

Official English text of the problem.

Answers

- **a)** From energy conservation, $m_\mu = 1.8835 \times 10^{-28}$ kg. The stated event has a momentum-conservation inconsistency: the electron's momentum, $p_e c = 1.49 \times 10^{-11}$ J, exceeds what the two neutrinos can carry, $c |\mathbf{p}_{\bar{\nu}_e} + \mathbf{p}_{\nu_\mu}| \leq 2.000 \times 10^{-12}$ J.
- **b)** $m_\mu = 1.884 \times 10^{-28}$ kg, including the finite mass of the proton.

Solution

The problem gives no numerical physical constants. We use the standard values

$$\begin{aligned}c &= 2.99792458 \times 10^8 \text{ m s}^{-1}, \\m_e &= 9.1093837 \times 10^{-31} \text{ kg}, \\m_p &= 1.6726219 \times 10^{-27} \text{ kg}, \\R_\infty &= 1.09737316 \times 10^7 \text{ m}^{-1}.\end{aligned}$$

a)

The decay, with the particle charges shown explicitly, is

$$\mu^- \longrightarrow e^- + \bar{\nu}_e + \nu_\mu.$$

Because the initial muon is stationary, its total energy is its rest energy, $m_\mu c^2$. The final electron carries both rest energy and kinetic energy. Hence

$$m_\mu c^2 = m_e c^2 + K_e + E_{\bar{\nu}_e} + E_{\nu_\mu}.$$

The stated neutrino energy is already their combined total energy, so

$$m_\mu = m_e + \frac{K_e + E_{\text{neutrinos}}}{c^2}.$$

Substitution gives

$$\begin{aligned} m_\mu &= 9.1093837 \times 10^{-31} \text{ kg} + \frac{1.4846 \times 10^{-11} + 2.000 \times 10^{-12}}{(2.99792458 \times 10^8)^2} \text{ kg} \\ &= \boxed{1.8835 \times 10^{-28} \text{ kg}}. \end{aligned}$$

This is approximately $206.76 m_e$.

b)

The $^1\text{H}^+$ nucleus is a proton (hydrogen-1 ion; SMILES [1H+]). Together with the bound negative muon, it forms muonic hydrogen. Standard SMILES cannot represent a muon or its orbital state.

Both particles move about their common centre of mass, so the hydrogen-like energy levels depend on the **reduced mass**

$$m_r = \frac{m_\mu m_p}{m_\mu + m_p},$$

rather than on m_μ alone. For nuclear charge $Z = 1$,

$$E_n = -hcR_\infty \frac{m_r}{m_e} \frac{1}{n^2}.$$

The ground state has $n = 1$; therefore the third excited state is $n = 4$, and the first excited state is $n = 2$. For the emitted photon,

$$\frac{hc}{\lambda} = E_4 - E_2 = hcR_\infty \frac{m_r}{m_e} \left(\frac{1}{2^2} - \frac{1}{4^2} \right).$$

Since the bracket equals $3/16$,

$$\frac{1}{\lambda} = \frac{3}{16} R_\infty \frac{m_r}{m_e}.$$

Thus

$$\begin{aligned} m_r &= \frac{16m_e}{3R_\infty \lambda} \\ &= \frac{16(9.1093837 \times 10^{-31})}{3(1.09737316 \times 10^7)(2.615 \times 10^{-9})} \text{ kg} \\ &= 1.6930185 \times 10^{-28} \text{ kg}. \end{aligned}$$

Solving the reduced-mass relation for the muon mass,

$$\frac{1}{m_\mu} = \frac{1}{m_r} - \frac{1}{m_p}, \quad m_\mu = \frac{m_r m_p}{m_p - m_r}.$$

Consequently,

$$m_\mu = \frac{(1.6930185 \times 10^{-28})(1.6726219 \times 10^{-27})}{1.6726219 \times 10^{-27} - 1.6930185 \times 10^{-28}} = \boxed{1.884 \times 10^{-28} \text{ kg}}.$$

The solution was checked against the official solution.

Problem 26: Spectrum of CO

PROBLEM 26 Spectrum of CO

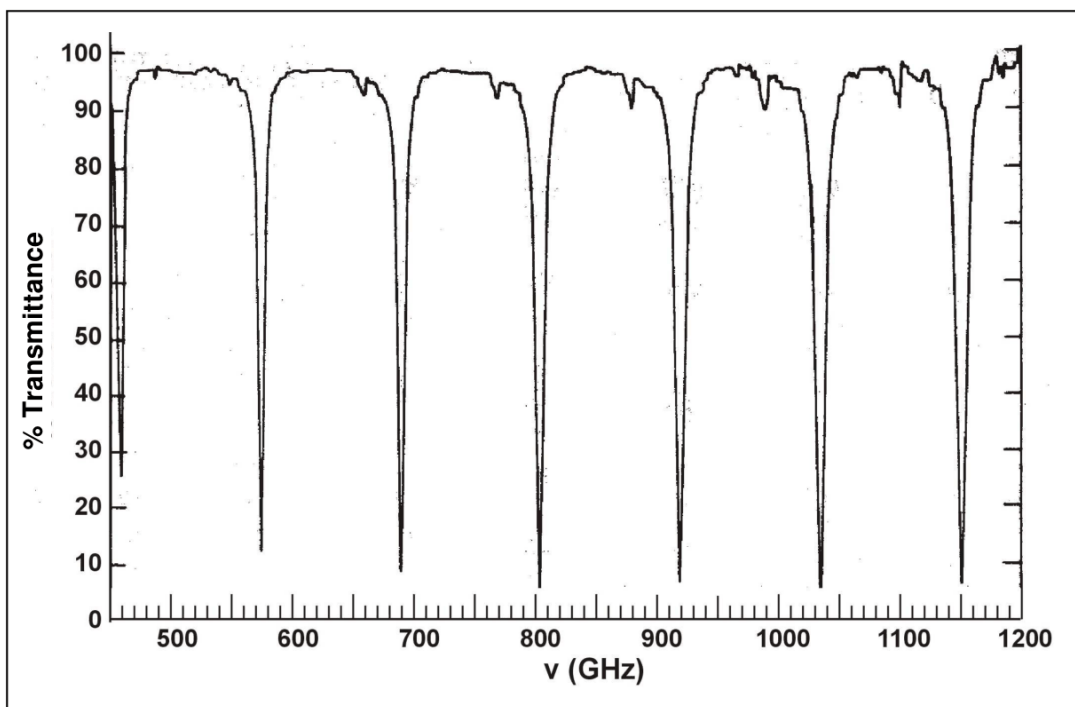
Rotational energy levels of diatomic molecules are well described by the formula $E_J = B J(J + 1)$, where J is the rotational quantum number of the molecule and B its rotational constant. Constant B is related to the reduced mass μ and the bond length R of the molecule through the equation

$$B = \frac{h^2}{8\pi^2 \mu R^2}.$$

In general, spectroscopic transitions appear at photon energies which are equal to the energy difference between appropriate states of a molecule ($h\nu = \Delta E$). The observed rotational transitions occur between adjacent rotational levels, hence $\Delta E = E_{J+1} - E_J = 2B(J + 1)$. Consequently, successive rotational transitions that appear on the spectrum (such as the one shown here) follow the equation $h(\Delta\nu) = 2B$.

By inspecting the spectrum provided, determine the following quantities for $^{12}\text{C}^{16}\text{O}$ with appropriate units:

- $\Delta\nu$
- B
- R



Official English text of the problem.

Answers

- a) $\Delta\nu \approx 115 \text{ GHz} = 1.15 \times 10^{11} \text{ Hz}$
- b) $B \approx 3.81 \times 10^{-23} \text{ J}$
- c) $R \approx 1.13 \times 10^{-10} \text{ m} = 113 \text{ pm}$

Solution

The molecule is carbon monoxide, $^{12}\text{C}^{16}\text{O}$, with isotopic SMILES `[12C-]#[16O+]`.

a) Frequency spacing, $\Delta\nu$

The strong absorption lines appear as minima in transmittance. From the spectrum, the minima near 460 and 1150 GHz span six successive intervals. Thus,

$$\Delta\nu \approx \frac{1150 - 460}{6} \text{ GHz} = 115 \text{ GHz} = 1.15 \times 10^{11} \text{ s}^{-1}.$$

b) Rotational constant, B

For the transition $J \rightarrow J + 1$,

$$h\nu_J = B[(J + 1)(J + 2) - J(J + 1)] = 2B(J + 1).$$

Therefore, adjacent spectral lines have spacing

$$\Delta\nu = \nu_{J+1} - \nu_J = \frac{2B}{h}.$$

Using the standard Planck constant $h = 6.62607015 \times 10^{-34} \text{ J s}$,

$$B = \frac{h\Delta\nu}{2} = \frac{(6.62607015 \times 10^{-34} \text{ J s})(1.15 \times 10^{11} \text{ s}^{-1})}{2} \approx \boxed{3.81 \times 10^{-23} \text{ J}}.$$

Here B has energy units, as defined in the problem.

c) Bond length, R

Approximating the isotope masses by $12u$ and $16u$, the reduced mass is

$$\mu = \frac{m_C m_O}{m_C + m_O} = \frac{12 \times 16}{12 + 16} u = 6.85714 u.$$

Using the standard conversion $u = 1.66054 \times 10^{-27} \text{ kg}$,

$$\mu \approx 1.13866 \times 10^{-26} \text{ kg}.$$

Rearranging the given expression for B ,

$$R = \sqrt{\frac{h^2}{8\pi^2 \mu B}} = \sqrt{\frac{(6.62607 \times 10^{-34} \text{ J s})^2}{8\pi^2 (1.13866 \times 10^{-26} \text{ kg})(3.80999 \times 10^{-23} \text{ J})}}.$$

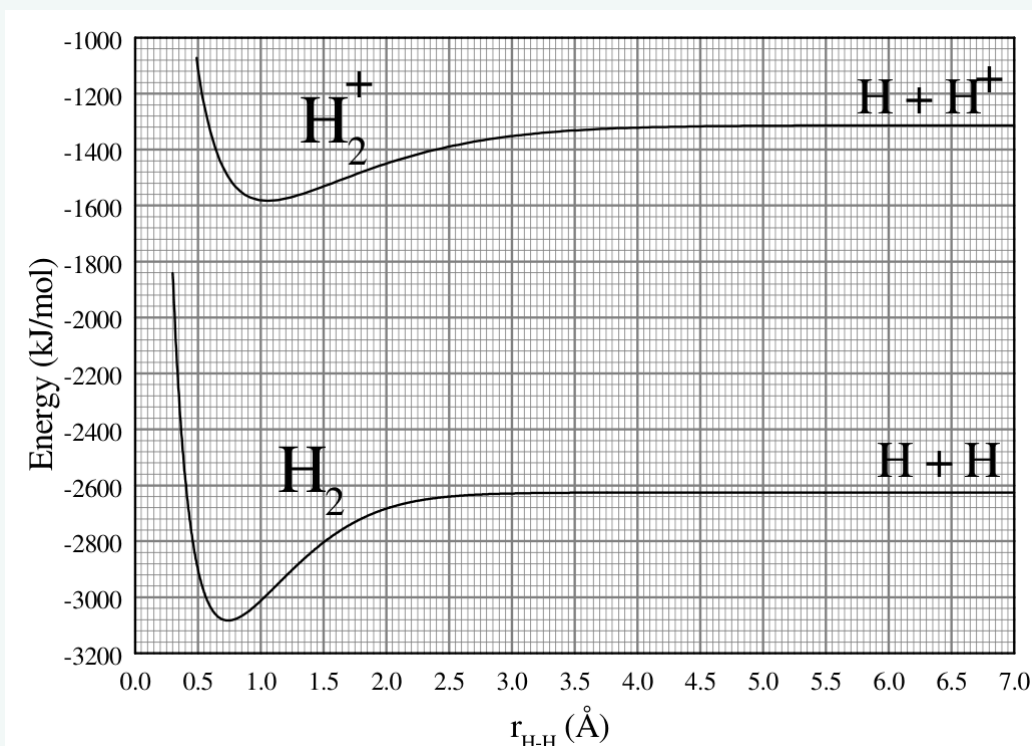
Hence,

$$\boxed{R \approx 1.13 \times 10^{-10} \text{ m} = 113 \text{ pm}}.$$

The solution was checked against the official solution.

Problem 27: Hydrogen molecule

Using the information provided on this graph, give numerical answers with appropriate units to the following questions:



1. What are the equilibrium bond lengths of H_2 and H_2^+ ?

- What are the binding energies of H_2 and H_2^+ ?
- What is the ionisation energy of the H_2 molecule?
- What is the ionisation energy of the H atom?
- If we use electromagnetic radiation of frequency $3.9 \times 10^{15} \text{ Hz}$ in order to ionise H_2 , what will be the velocity of the extracted electrons? (Ignore molecular vibrational energy.)

Official English text of the problem.

Answers

- Molecular hydrogen, H_2 ([H][H]): $r_e \approx 0.75 \text{ \AA}$. Dihydrogen cation, H_2^+ ([H][H+]): $r_e \approx 1.05 \text{ \AA}$.
- $D_e(\text{H}_2) \approx 460 \text{ kJ mol}^{-1}$; $D_e(\text{H}_2^+) \approx 270 \text{ kJ mol}^{-1}$.
- $I(\text{H}_2) \approx 1500 \text{ kJ mol}^{-1}$.
- $I(\text{H}) \approx 1310 \text{ kJ mol}^{-1}$.
- Electron speed: $v \approx 4.5 \times 10^5 \text{ m s}^{-1}$.

Solution

The approximate energy readings used below are:

Curve	Minimum energy / kJ mol^{-1}	Energy at infinite separation / kJ mol^{-1}
H_2	-3080	-2620, corresponding to $\text{H} + \text{H}$
H_2^+	-1580	-1310, corresponding to $\text{H} + \text{H}^+$

Here, H is a hydrogen atom ([H]), and H^+ is a proton ([H+]). The SMILES given for H_2^+ specifies connectivity and charge; it does not express its one-electron bond, whose bond order is 1/2.

1. Equilibrium bond lengths

The equilibrium separation is the position of the minimum of each potential-energy curve: shortening or lengthening the bond from this position increases its energy.

Reading the horizontal coordinates of the minima gives

$$r_e(\text{H}_2) \approx 0.75 \text{ \AA}, \quad r_e(\text{H}_2^+) \approx 1.05 \text{ \AA}.$$

2. Binding energies

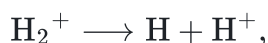
The binding energy is the positive energy required to separate the equilibrium molecule into the fragments shown at its dissociation limit.

For molecular hydrogen,

$$\text{H}_2 \longrightarrow \text{H} + \text{H},$$

$$D_e(\text{H}_2) = E(\text{H} + \text{H}) - E_{\min}(\text{H}_2) \approx -2620 - (-3080) = 460 \text{ kJ mol}^{-1}.$$

For the dihydrogen cation,



$$D_e(\text{H}_2^+) = E(\text{H} + \text{H}^+) - E_{\min}(\text{H}_2^+) \approx -1310 - (-1580) = \boxed{270 \text{ kJ mol}^{-1}}.$$

3. Ionisation energy of the hydrogen molecule

The ionisation process is



Taking the molecule and molecular ion at their respective equilibrium geometries, and the removed electron at rest at infinity, the ionisation energy is the difference between the two curve minima:

$$I(\text{H}_2) = E_{\min}(\text{H}_2^+) - E_{\min}(\text{H}_2) \approx -1580 - (-3080) = \boxed{1500 \text{ kJ mol}^{-1}}.$$

4. Ionisation energy of the hydrogen atom

Atomic ionisation is

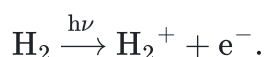


The two dissociation limits differ by precisely this process: one hydrogen atom remains unchanged while the other is ionised. Therefore,

$$I(\text{H}) = E(\text{H} + \text{H}^+) - E(\text{H} + \text{H}) \approx -1310 - (-2620) = \boxed{1310 \text{ kJ mol}^{-1}}.$$

5. Velocity of the extracted electrons

Photoionisation occurs according to



Ignoring molecular vibrational energy and the negligible kinetic energy of ion recoil, conservation of energy gives

$$h\nu = \frac{I(\text{H}_2)}{N_A} + \frac{1}{2}m_e v^2.$$

Using the standard constants

$$h = 6.626 \times 10^{-34} \text{ J s}, \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1}, \quad m_e = 9.109 \times 10^{-31} \text{ kg},$$

the photon energy is

$$E_\gamma = (6.626 \times 10^{-34})(3.9 \times 10^{15}) = 2.584 \times 10^{-18} \text{ J}.$$

The ionisation energy per molecule is

$$E_{\text{ion}} = \frac{1500 \times 10^3}{6.022 \times 10^{23}} = 2.491 \times 10^{-18} \text{ J}.$$

Thus the electron receives kinetic energy

$$K_e = E_\gamma - E_{\text{ion}} \approx 9.3 \times 10^{-20} \text{ J},$$

and its speed is

$$v = \sqrt{\frac{2K_e}{m_e}} \approx \sqrt{\frac{2(9.3 \times 10^{-20})}{9.109 \times 10^{-31}}} = \boxed{4.5 \times 10^5 \text{ m s}^{-1}}.$$

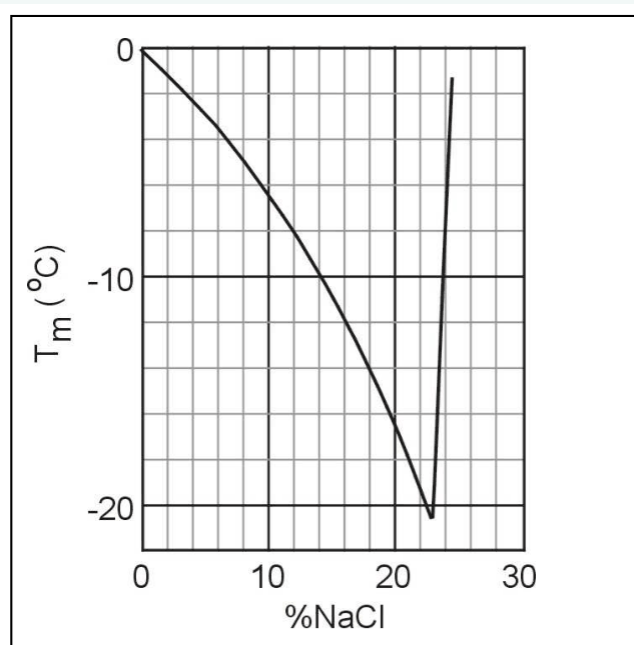
The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 28: Cryoscopy

Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point ($0\text{ }^{\circ}\text{C}$) and well above the CO_2 sublimation point ($-78\text{ }^{\circ}\text{C}$) this case they mix water ice prepared at its melting point and NaCl . Depending on the quantities used temperatures as low as $-20\text{ }^{\circ}\text{C}$ can be reached.

We prepare a cold bath mixing 1 kg of ice at $0\text{ }^{\circ}\text{C}$ with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

- a) The mixing process is spontaneous. (Y) (N)
- b) The change of entropy during the mixing process is negative. (Y) (N)
- c) The following diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is the freezing point of the bath based on the diagram?



- d) If an equal mass of MgCl_2 were used instead of NaCl , would the freezing point be higher? (Y) (N)

Official English text of the problem.

Answers

- a) Y.
- b) N. The entropy of the insulated system increases.
- c) **Approximately** $-9\text{ }^{\circ}\text{C}$, using the overall composition of 13.0% NaCl by mass.
- d) Y, under the usual ideal, complete-dissociation cryoscopic model.

Solution

a) Water, H_2O (o), is initially present as solid ice at its melting point. Dissolved salt lowers the chemical potential of liquid water, making melting into the salt solution favorable. Salt dissolution and ice melting therefore proceed spontaneously.

Melting absorbs energy. Because the container is thermally insulated, this energy comes from the bath itself, causing its temperature to fall.

b) For the entire insulated system, there is no entropy transfer through heat exchange with the surroundings. Consequently,

$$\Delta S_{\text{system}} = S_{\text{generated}} > 0$$

for this spontaneous, irreversible process.

The entropy gains associated with mixing and melting outweigh the entropy decrease associated with cooling. Thus the statement that the entropy change is negative is **false**.

c) Taking the stated quantities as the composition of the resulting solution, the mass percentage of salt is

$$w(\text{NaCl}) = \frac{m(\text{NaCl})}{m(\text{NaCl}) + m(\text{H}_2\text{O})} \times 100\% = \frac{150 \text{ g}}{150 \text{ g} + 1000 \text{ g}} \times 100\% = 13.0\%.$$

At 13.0% on the horizontal axis, the descending branch of the graph gives approximately

$$T_f \approx -9^\circ \text{C}.$$

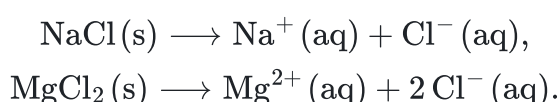
This is the freezing point associated with the stated **overall solution composition**.

d) Freezing-point depression depends on the number of dissolved particles per unit mass of solvent:

$$\Delta T_f = i K_f b,$$

where i is the van 't Hoff factor and b is the formula-unit molality.

The ideal dissociation equations are



Thus $i = 2$ for sodium chloride and $i = 3$ for magnesium chloride. The dissolved species are sodium ion ([Na+]), magnesium ion ([Mg+2]) and chloride ion ([Cl-]); these SMILES do not represent their hydration shells.

Using the standard approximate molar masses

$$M(\text{NaCl}) = 58.44 \text{ g mol}^{-1}, \quad M(\text{MgCl}_2) = 95.21 \text{ g mol}^{-1},$$

the amounts of dissolved particles produced by 150 g are

$$\begin{aligned}n_{\text{particles}}(\text{NaCl}) &= 2 \frac{150 \text{ g}}{58.44 \text{ g mol}^{-1}} = 5.13 \text{ mol}, \\ n_{\text{particles}}(\text{MgCl}_2) &= 3 \frac{150 \text{ g}}{95.21 \text{ g mol}^{-1}} = 4.73 \text{ mol}.\end{aligned}$$

For equal solvent masses,

$$\frac{\Delta T_f(\text{MgCl}_2)}{\Delta T_f(\text{NaCl})} = \frac{4.73}{5.13} \approx 0.921.$$

An equal mass of magnesium chloride therefore gives fewer dissolved particles and a smaller freezing-point depression. Its freezing point is **higher**, so the answer is **Y**.

The solution was checked against the official solution.

Problem 29: Pool

A very large swimming pool filled with water of temperature equal to 20 °C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine:

- a) The heat delivered to the water.
- b) Is the change of entropy of the resistor positive, negative, or zero?
 - (i) $\Delta S_{\text{res}} > 0$ ()
 - (ii) $\Delta S_{\text{res}} = 0$ ()
 - (iii) $\Delta S_{\text{res}} < 0$ ()
- c) Is the change of entropy of the water positive, negative, or zero?
 - i) $\Delta S_{\text{pool}} > 0$ ()
 - (ii) $\Delta S_{\text{pool}} = 0$ ()
 - (iii) $\Delta S_{\text{pool}} < 0$ ()
- d) Is the change of entropy of the system positive, negative, or zero?
 - (i) $\Delta S_{\text{total}} > 0$ ()
 - (ii) $\Delta S_{\text{total}} = 0$ ()
 - (iii) $\Delta S_{\text{total}} < 0$ ()
- e) Is the process reversible? (Y) (N)

Official English text of the problem.

Answers

- **a)** $Q_{\text{water}} = 6.0 \times 10^5 \text{ J} = 6.0 \times 10^2 \text{ kJ}$.
- **b)** Select **(ii)**: $\Delta S_{\text{res}} = 0$, assuming steady operation.
- **c)** Select **(i)**: $\Delta S_{\text{pool}} > 0$.
- **d)** Select **(i)**: $\Delta S_{\text{total}} > 0$.
- **e)** Select **N**: the process is irreversible.

Solution

a) The heat delivered equals the heating power multiplied by the operating time:

$$t = 20 \times 60 = 1200 \text{ s},$$
$$Q_{\text{water}} = Pt = (500 \text{ J s}^{-1})(1200 \text{ s}) = \boxed{6.0 \times 10^5 \text{ J}}.$$

b) In the intended steady-operation model, the resistor continuously receives electrical work and transfers the resulting energy to the water as heat. Its temperature and thermodynamic state remain constant. Since entropy is a state function,

$$\boxed{\Delta S_{\text{res}} = 0}.$$

This does not mean that no entropy is generated inside the resistor. Joule heating generates entropy, which is continuously transferred to the water with the heat; there is no net accumulation in the resistor.

c) The water receives heat and its entropy increases. Because the pool is very large, its temperature changes negligibly, so it can be treated approximately as a heat reservoir at

$$T_{\text{pool}} = 20 + 273.15 = 293.15 \text{ K}.$$

Evaluating the entropy change using a reversible heat-transfer path between the same states gives

$$\Delta S_{\text{pool}} \approx \frac{Q_{\text{water}}}{T_{\text{pool}}} = \frac{6.0 \times 10^5 \text{ J}}{293.15 \text{ K}} \approx 2.0 \times 10^3 \text{ J K}^{-1} > 0.$$

Thus,

$$\boxed{\Delta S_{\text{pool}} > 0}.$$

A small actual temperature rise would change the numerical approximation, but not the positive sign.

d) Taking the system to consist of the resistor and the pool,

$$\Delta S_{\text{total}} = \Delta S_{\text{res}} + \Delta S_{\text{pool}} = 0 + \Delta S_{\text{pool}} > 0.$$

Therefore,

$$\boxed{\Delta S_{\text{total}} > 0}.$$

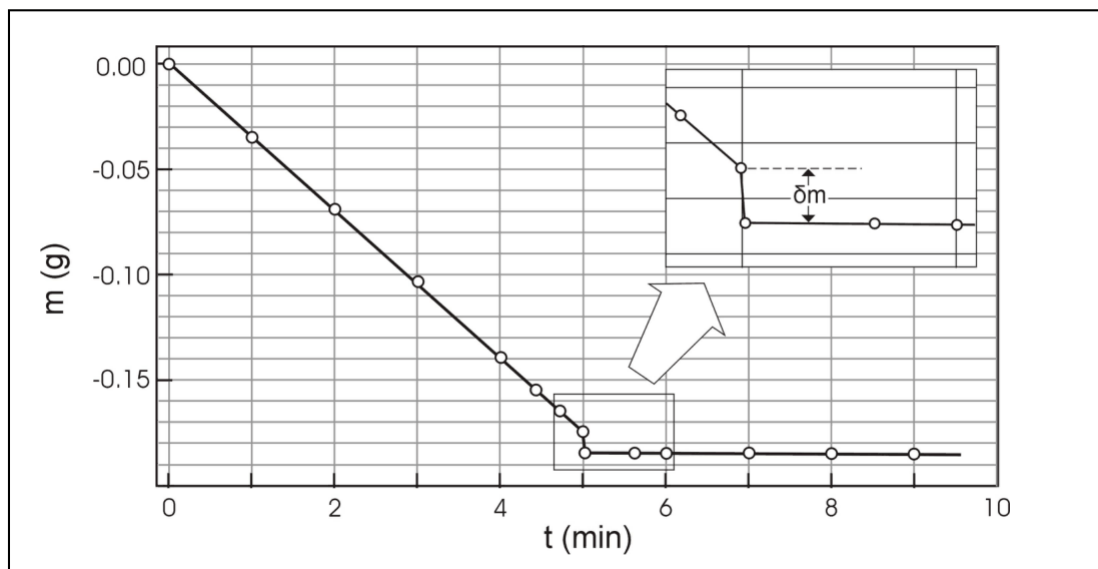
Electrical work supplies energy without transferring entropy. The increase in total entropy results from irreversible dissipation.

e) A reversible process generates no entropy. Here electrical energy is dissipated by Joule heating, producing a positive total entropy change. Therefore, the process is **irreversible**, and **N** must be selected.

The solution was checked against the official solution.

Problem 30: Gas velocity

The experiment described here gives a simple way to determine the mean velocity u of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time $t = 0$. Balance readings are recorded as shown on the diagram.



At $t = 5$ min the lid is placed over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δm . Therefore, the force exerted on the lid is $f = \delta m g$. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., $f = \frac{1}{2} u \frac{dm}{dt}$. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume $g = 9.8 \text{ m s}^{-2}$.

Official English text of the problem.

Answers

- **30.** The mean molecular speed of ethanol at 290 K is approximately

$$u = 3.4 \times 10^2 \text{ m s}^{-1}.$$

Solution

30. Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, has SMILES `cco`.

The graph's straight-line slope before the lid is placed gives the evaporation rate. The balance reading falls from 0.000 g to approximately -0.175 g over 5.0 min. Taking the positive magnitude of the mass-loss rate,

$$\dot{m}_{\text{evap}} = \frac{0.175 \text{ g}}{5.0 \text{ min}} = 0.035 \text{ g min}^{-1} = \frac{0.035 \times 10^{-3}}{60} \text{ kg s}^{-1} = 5.83 \times 10^{-7} \text{ kg s}^{-1}.$$

At lid closure, the reading drops from approximately -0.175 g to -0.185 g. Thus,

$$\delta m = (-0.175) - (-0.185) = 0.010 \text{ g} = 1.0 \times 10^{-5} \text{ kg}.$$

Using the force relation supplied in the problem,

$$f = \delta m g = (1.0 \times 10^{-5} \text{ kg})(9.8 \text{ m s}^{-2}) = 9.8 \times 10^{-5} \text{ N}.$$

Equating this to the stated rate of momentum transfer,

$$\delta m g = \frac{1}{2} u \dot{m}_{\text{evap}},$$

so

$$u = \frac{2\delta m g}{\dot{m}_{\text{evap}}} = \frac{2(9.8 \times 10^{-5} \text{ N})}{5.83 \times 10^{-7} \text{ kg s}^{-1}} = 3.36 \times 10^2 \text{ m s}^{-1}.$$

To sensible precision for the graphical data, the mean molecular speed at 290 K is

$$u \approx 3.4 \times 10^2 \text{ m s}^{-1}.$$

The solution was checked against the official solution.

Problem 31: Ester identification

SECTION C: Organic Chemistry

PROBLEM 31 Ester identification

2.81 g of an optically active diester **A**, containing only C, H and O were saponified with 30.00 cm³ of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 cm³ of a 1.00 M HCl solution to titrate the unused NaOH only. The saponification products were an optically inactive dicarboxylic acid **B**, MeOH and an optically active alcohol **C**. Alcohol **C** reacted with I₂/NaOH to give a yellow precipitate and C₆H₅COONa. The diacid **B** reacted with Br₂ in CCl₄ to give a single, optically inactive product (compound **D**). Ozonolysis of **B** gave only one product.

- Determine the molecular mass of compound **A**.
- Give the structural formulas of **A**, **B**, and **C** without stereochemical information.
- Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.
- Give the stereochemical formula for **D**, using a Fischer projection.
- Give the stereochemical formula for **B**.

The diester **A** also reacted with Br₂ in CCl₄ and was converted to a mixture of two compounds (**E**, **F**) both optically active.

- Give all the possible stereochemical formulas for **E** and **F**, using Fischer projections. Name all the stereogenic centers as either *R* or *S* on all the formulas.

If we use Na¹⁸OH for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

- Mark the correct answer:

- Only **B** ()
- Only **C** ()
- Both **B** and **C** ()

Official English text of the problem.

Answers

- **a)** $M_r(\mathbf{A}) = 234$, corresponding to a molar mass of 234 g mol^{-1} .
- **b)** Structures without stereochemical information:
 - **A:** methyl 1-phenylethyl but-2-enedioate, COC(=O)C=CC(=O)OC(C)c1ccccc1.
 - **B:** but-2-enedioic acid, O=C(O)C=CC(=O)O.
 - **C:** 1-phenylethanol, CC(O)c1ccccc1.
- **c)** The possibilities are **(R)-1-phenylethanol**, C[C@H](O)c1ccccc1, and **(S)-1-phenylethanol**, C[C@@H](O)c1ccccc1. Their wedge-and-dash descriptions are given below.
- **d)** **D** is **meso-(2R,3S)-2,3-dibromobutanedioic acid**, O=C(O)[C@H](Br)[C@@H](Br)C(=O)O. Its Fischer projection has both bromine atoms on the same side.
- **e)** **B** is **fumaric acid**, **(E)-but-2-enedioic acid**, O=C(O)/C=C/C(=O)O: the carboxyl groups are trans.
- **f)** Numbering the butanedioate chain from the methyl-ester end and calling the original alcohol stereocentre $1'$, the four possible configurations are
 $(2R, 3S, 1'R), (2S, 3R, 1'R), (2R, 3S, 1'S), (2S, 3R, 1'S)$.
 For either fixed configuration at $1'$, the corresponding two products are diastereomers. Their complete names, SMILES and Fischer placements appear below.
- **g)** i) Only B.

Solution

a) Molecular mass of A

The back-titration measures the remaining sodium hydroxide:



Here sodium hydroxide is $[\text{Na}^+] \cdot [\text{OH}^-]$, hydrogen chloride is Cl , sodium chloride is $[\text{Na}^+] \cdot [\text{Cl}^-]$, and water is O .

The initial and remaining amounts of base are

$$\begin{aligned} n_{\text{initial}}(\text{NaOH}) &= (30.00 \times 10^{-3} \text{ L})(1.00 \text{ mol L}^{-1}) = 0.0300 \text{ mol}, \\ n_{\text{remaining}}(\text{NaOH}) &= (6.00 \times 10^{-3} \text{ L})(1.00 \text{ mol L}^{-1}) = 0.00600 \text{ mol}. \end{aligned}$$

Thus,

$$n_{\text{consumed}}(\text{NaOH}) = 0.0240 \text{ mol}.$$

Each molecule of a diester consumes two equivalents of hydroxide:

$$n(\mathbf{A}) = \frac{0.0240}{2} = 0.0120 \text{ mol}.$$

Therefore,

$$M(\mathbf{A}) = \frac{2.81 \text{ g}}{0.0120 \text{ mol}} = 234 \text{ g mol}^{-1}.$$

b) Constitutional structures of A, B and C

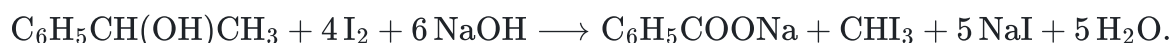
The yellow precipitate is **iodoform**, $\text{IC}(\text{I})\text{I}$. An optically active alcohol undergoing the iodoform reaction contains the unit $\text{CH}_3-\text{CH}(\text{OH})-\text{R}$. Formation of **sodium benzoate**, $[\text{Na}^+]$.

$[\text{O}^-]\text{C}(=\text{O})\text{c1ccccc1}$, identifies the other substituent as phenyl.

Consequently, **C** is **1-phenylethanol**:



Its balanced iodoform reaction is



Iodine has SMILES II ; sodium iodide has SMILES $[\text{Na}^+] \cdot [\text{I}^-]$.

The other alcohol is **methanol**, CO . Formation of the diester from the diacid and the two alcohols eliminates two water molecules, so

$$M(\mathbf{A}) = M(\mathbf{B}) + M(\text{CH}_3\text{OH}) + M(\mathbf{C}) - 2M(\text{H}_2\text{O}).$$

Using the nominal formula masses,

$$M(\mathbf{B}) \approx 234 + 2(18) - 32 - 122 = 116 \text{ g mol}^{-1}.$$

A dicarboxylic acid of this mass, containing only carbon, hydrogen and oxygen, has molecular formula $\text{C}_4\text{H}_4\text{O}_4$. Its degree of unsaturation is

$$\text{DBE} = \frac{2(4) + 2 - 4}{2} = 3.$$

Two units arise from the carboxyl carbonyls; the third corresponds to the alkene that reacts with bromine. Obtaining only one organic product upon ozonolysis identifies equivalent alkene halves:

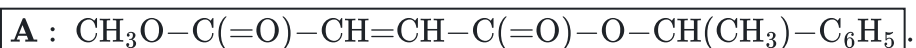


For example, a conventional reductive ozonolysis gives two molecules of **glyoxylic acid (2-oxoacetic acid)**, $\text{O}=\text{CC}(=\text{O})\text{O}$:



This balanced equation uses dimethyl sulfide as the reductive work-up reagent. Ozone is $[\text{O}^-][\text{O}^+]=\text{O}$, dimethyl sulfide is CSC , and dimethyl sulfoxide is $\text{CS}(\text{C})=\text{O}$. The work-up itself is not specified in the question.

Combining **B**, methanol and **C** gives



Its molecular formula is $\text{C}_{13}\text{H}_{14}\text{O}_4$, consistent with the measured molar mass:

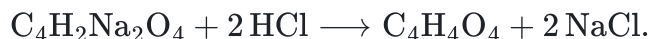
$$13(12) + 14(1) + 4(16) = 234.$$

The balanced saponification equation is



The actual alkaline product is **disodium but-2-enedioate**, $[\text{Na}^+] \cdot [\text{Na}^+] \cdot [\text{O}^-]\text{C}(=\text{O})\text{C}=\text{CC}(=\text{O})[\text{O}^-]$.

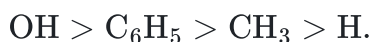
The diacid **B** is obtained on subsequent acidification:



This acidification is separate from the stated back-titration, which measures unused hydroxide only.

c) Possible stereochemical formulas of C

The alcohol carbon is attached to four different groups. Its CIP priorities are



Thus **C** can have either the *R* or the *S* configuration; the information supplied does not select between them.

For precise wedge-and-dash drawings, put the stereogenic carbon at the centre, with phenyl at the upper left and methyl at the upper right, both connected by ordinary bonds in the plane:

- **(R)-1-phenylethanol**: put OH at the lower left on a **solid wedge toward the observer**, and H at the lower right on a **dashed wedge away**.
- **(S)-1-phenylethanol**: retain those positions but reverse the wedge types: OH is dashed away, and H is solid toward the observer.

These are the two enantiomers whose stereochemical SMILES are listed in the Answers.

d) Fischer projection of D

Bromination adds two bromine atoms across the double bond:



Bromine is BrBr; the solvent, carbon tetrachloride, is ClC(Cl)(Cl)Cl.

Addition is **anti**. The single optically inactive stereoisomer is therefore **meso-2,3-dibromobutanedioic acid**.

Describe its Fischer projection as follows:

- Put the four-carbon chain vertically, with COOH at both the top and bottom.
- At each of the two stereogenic carbons, put Br on the **left** and H on the **right**.
- Horizontal bonds point toward the observer; vertical bonds point away.

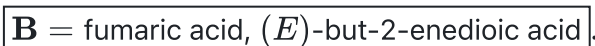
Numbering from the top gives **C2** *R* and **C3** *S*. At either centre, the priorities are



The internal symmetry makes this molecule achiral despite its two stereogenic centres.

e) Stereochemical formula of B

Anti addition to the **trans** alkene produces the meso dibromide found in part (d). Hence

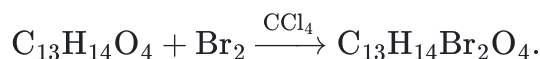


For its drawing, place the double bond horizontally. Put COOH above the left alkene carbon and below the right alkene carbon; put the two hydrogens in the remaining positions.

Thus the two carboxyl groups lie on opposite sides of the double bond. Its stereochemical SMILES is O=C(O)/C=C/C(=O)O.

f) All possible stereochemical formulas of E and F

Saponification preserves the alkene configuration, so **A** is a mixed ester of fumaric acid. Its bromination has the balanced molecular equation



Anti addition generates the configurations (*2R, 3S*) or (*2S, 3R*) at the two new stereogenic centres. The existing 1-phenylethyl stereocentre retains its configuration.

Number the butanedioate chain from the **methyl-ester end**, and label the original alcohol stereocentre **C1'**. The product labels below are arbitrary.

Product	Complete name	Stereochemical SMILES
E_R	Methyl [(1 <i>R</i>)-1-phenylethyl] (2 <i>R,3S</i>)-2,3-dibromobutanedioate	<chem>COC(=O)[C@H](Br)[C@@H](Br)C(=O)O[C@H](C)c1ccccc1</chem>
F_R	Methyl [(1 <i>R</i>)-1-phenylethyl] (2 <i>S,3R</i>)-2,3-dibromobutanedioate	<chem>COC(=O)[C@H](Br)[C@H](Br)C(=O)O[C@H](C)c1ccccc1</chem>
E_S	Methyl [(1 <i>S</i>)-1-phenylethyl] (2 <i>R,3S</i>)-2,3-dibromobutanedioate	<chem>COC(=O)[C@@H](Br)[C@@H](Br)C(=O)O[C@@H](C)c1ccccc1</chem>
F_S	Methyl [(1 <i>S</i>)-1-phenylethyl] (2 <i>S,3R</i>)-2,3-dibromobutanedioate	<chem>COC(=O)[C@H](Br)[C@H](Br)C(=O)O[C@@H](C)c1ccccc1</chem>

For all four **Fischer projections**, use the following connected vertical sequence, from top to bottom:



Here Ph denotes the phenyl group, C_6H_5 . Complete the horizontal bonds according to this table; each entry specifies **left / right**, followed by the centre's configuration.

Product	At C2	At C3	At C1'
E_R	Br/H, <i>R</i>	Br/H, <i>S</i>	Ph/H, <i>R</i>
F_R	H/Br, <i>S</i>	H/Br, <i>R</i>	Ph/H, <i>R</i>
E_S	Br/H, <i>R</i>	Br/H, <i>S</i>	H/Ph, <i>S</i>
F_S	H/Br, <i>S</i>	H/Br, <i>R</i>	H/Ph, <i>S</i>

As usual, horizontal Fischer bonds project toward the observer and vertical bonds away.

For an **A** enantiomer with 1'*R*, the products are E_R and F_R ; for 1'*S*, they are E_S and F_S . Each pair consists of diastereomers. Across the two pairs, E_R/F_S and F_R/E_S are enantiomeric pairs.

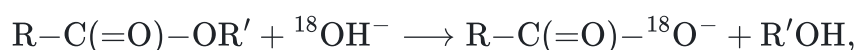
g) Incorporation of oxygen-18

The correct choice is

i) Only B.

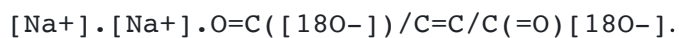
Saponification proceeds by nucleophilic acyl substitution. Hydroxide attacks the ester carbonyl carbon; collapse of the tetrahedral intermediate breaks the bond between the acyl carbon and the original alkoxy oxygen. That original oxygen remains with the alcohol.

For either ester group, the isotope accounting is



where R and R' denote the corresponding organic groups.

Thus oxygen-18-labelled sodium hydroxide, $[\text{Na}^+] \cdot [^{18}\text{OH}^-]$, introduces oxygen-18 into the carboxylate groups of **B**. A representation of **disodium fumarate labelled once in each carboxylate group** is

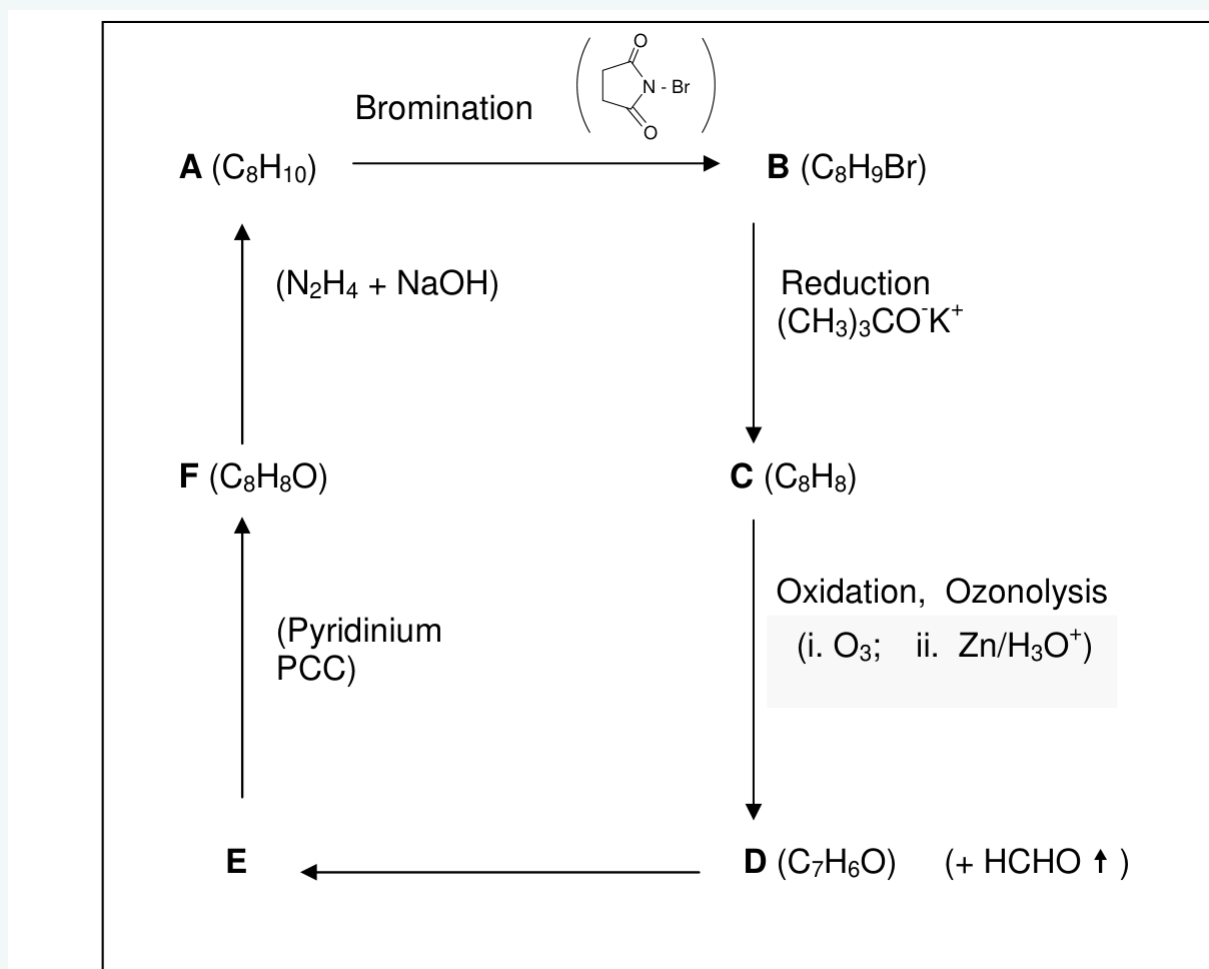


Acidification retains the labels in **B**. Alcohol **C** retains its original ester oxygen and does not acquire the isotope through this mechanism.

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 32: NMR puzzle

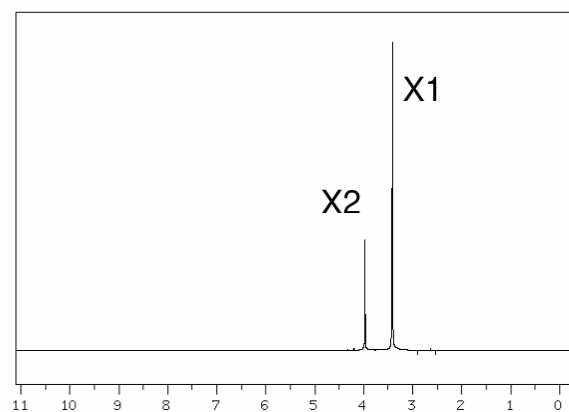
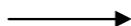
An organic compound **A** (C_8H_{10}) gives the following chain of reactions:

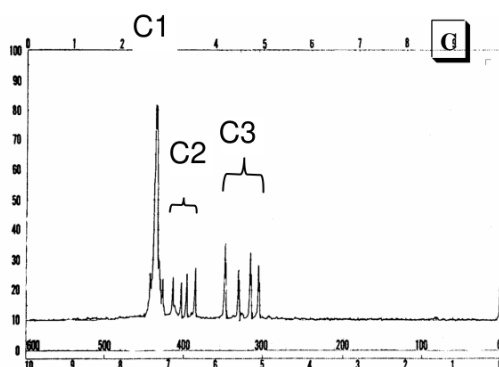
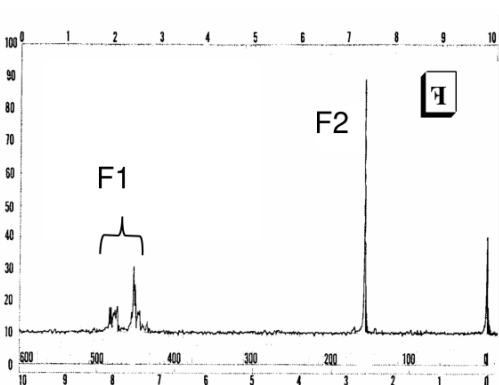
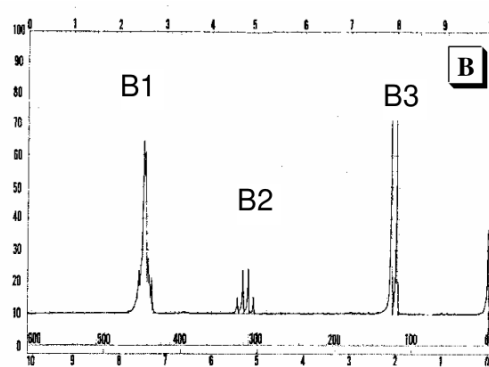
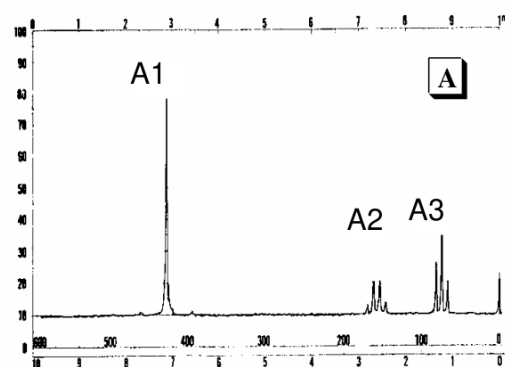


Based on the ^1H -NMR spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding ^1H -NMR peaks, as shown in the example.

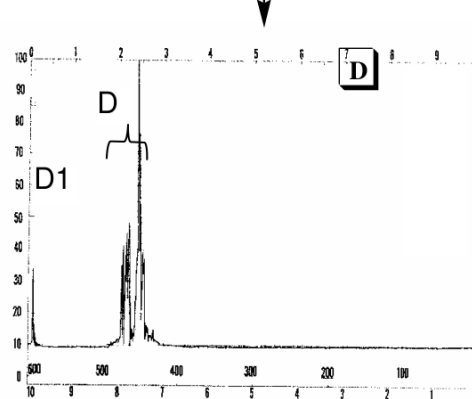
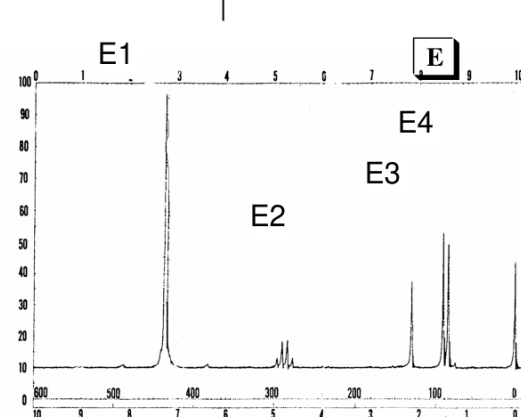
EXAMPLE

X1 X2
CH₃OH





Integration 5 : 1 : 2



General remarks: NMR spectra were recorded in CDCl_3 on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in CDCl_3 solutions and catalyse rapid exchange of some particular protons.

Official English text of the problem.

Answers

The supplied problem has no numbered subparts or stated point values. The compound labels are retained below.

- **A — Ethylbenzene**, $C_6H_5CH_2CH_3$, SMILES CCc1ccccc1. **A1**: five aromatic H; **A2**: benzylic CH_2 , 2 H; **A3**: terminal CH_3 , 3 H.
- **B — (1-Bromoethyl)benzene**, $C_6H_5CH(Br)CH_3$, expected as a racemate. Enantiomer SMILES: C[C@H](Br)c1ccccc1 and C[C@@H](Br)c1ccccc1. **B1**: five aromatic H; **B2**: $CHBr$, 1 H; **B3**: CH_3 , 3 H.
- **C — Styrene (ethenylbenzene)**, $C_6H_5CH=CH_2$, SMILES C=Cc1ccccc1. **C1**: five aromatic H; **C2**: ring-adjacent vinylic CH , 1 H; **C3**: the two nonequivalent terminal vinylic H, 2 H total.
- **D — Benzaldehyde**, C_6H_5CHO , SMILES O=Cc1ccccc1. **D1**: aldehydic H, 1 H; **D2** (the aromatic bracket labelled "D" in the scan): five aromatic H.
- **E — 1-Phenylethanol**, $C_6H_5CH(OH)CH_3$, molecular formula $C_8H_{10}O$, expected as a racemate. Enantiomer SMILES: C[C@H](O)c1ccccc1 and C[C@@H](O)c1ccccc1. **E1**: five aromatic H; **E2**: $CH(OH)$, 1 H; **E3**: hydroxyl H, 1 H; **E4**: CH_3 , 3 H.
- **F — Acetophenone (1-phenylethan-1-one)**, $C_6H_5COCH_3$, SMILES CC(=O)c1ccccc1. **F1**: five aromatic H; **F2**: carbonyl-adjacent CH_3 , 3 H.

Solution

Chemical shifts below are approximate readings from the supplied spectra, in ppm. Each five-proton aromatic envelope contains the ortho, meta and para protons of a monosubstituted benzene ring; assigning them one label does not imply that all five are chemically equivalent.

A — Identification of the starting hydrocarbon

For C_8H_{10} , the degree of unsaturation is

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

This is consistent with a benzene ring. The spectrum identifies the remaining two carbons as an ethyl group:

Label	Approximate δ / ppm	Assignment	Multiplicity
A1	7.2	Five aromatic H	Aromatic envelope
A2	2.6	Benzylic CH_2 , 2 H	Quartet
A3	1.3	Terminal CH_3 , 3 H	Triplet

The methylene protons are split by three neighbouring methyl protons, while the methyl protons are split by two methylene protons. Thus **A is ethylbenzene**.

B — Benzylic bromination

The reagent drawn is **N-bromosuccinimide**, SMILES O=C1CCC(=O)N1Br. It replaces a benzylic hydrogen by bromine, giving **(1-bromoethyl)benzene**. The balanced reaction is



The other product is **succinimide**, SMILES O=C1CCC(=O)N1.

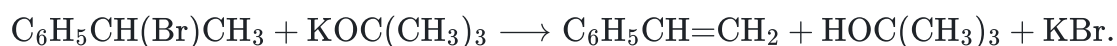
Label	Approximate δ / ppm	Assignment	Multiplicity
B1	7.2–7.6	Five aromatic H	Multiplet
B2	5.2	CHBr, 1 H	Quartet
B3	2.0	CH ₃ , 3 H	Doublet

Replacing a benzylic H with electronegative bromine shifts the remaining methine H substantially downfield. The methine is split by three methyl H, and the methyl group is split by one methine H.

A stereogenic centre is created. Under achiral radical bromination conditions, the product is expected to be racemic; the two enantiomers have identical spectra in the stated achiral solvent.

C — Elimination to form styrene

Potassium tert-butoxide, SMILES CC(C)(C)[O-].[K+], removes a hydrogen from the methyl group while bromide leaves the adjacent carbon. This is an E2 dehydrobromination:



The byproducts are **tert-butanol**, SMILES CC(C)(C)O, and **potassium bromide**, SMILES [K+].[Br-].

The arrow labelled "Reduction" in the scheme therefore represents an **elimination**. The product is **styrene**.

Label	Approximate δ / ppm	Assignment	Multiplicity
C1	7.2–7.5	Five aromatic H	Multiplet
C2	6.7	Ring-adjacent vinylic CH, 1 H	Approximately a doublet of doublets
C3	5.2 and 5.7	Terminal CH ₂ , 1 H at each position	Two approximately doublet-of-doublet patterns

This gives the stated integration:

$$\boxed{\text{C1} : \text{C2} : \text{C3} = 5 : 1 : 2}.$$

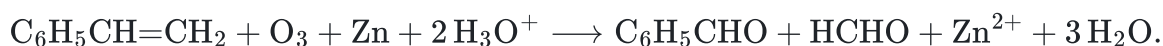
The two terminal alkene hydrogens are nonequivalent: one is cis and the other trans to the ring-adjacent vinylic hydrogen. They consequently have different chemical shifts and different vicinal coupling constants. C2 couples separately to both.

D — Reductive ozonolysis

Cleavage of the side-chain double bond produces one carbonyl compound from each alkene carbon:

- The ring-adjacent carbon gives **benzaldehyde, D**.
- The terminal carbon gives **methanal (formaldehyde)**, SMILES C=O.

A balanced net equation including the acidic zinc work-up is



The reductive work-up preserves the aldehyde products.

Label	Approximate δ / ppm	Assignment	Multiplicity
D1	10	Aldehydic CHO, 1 H	Approximately a singlet
D2, printed "D"	7.4–8.0	Five aromatic H	Multiplets

The characteristic aldehydic resonance and the formula C_7H_6O establish **D** as **benzaldehyde**.

E — Methyl addition to the aldehyde

The spectrum of E contains a methyl doublet, a methine quartet and an exchangeable hydroxyl proton. Together with five aromatic hydrogens, these identify **1-phenylethanol**.

It is obtained from D by addition of **methylmagnesium bromide**, SMILES C[Mg]Br, followed by acidic work-up:



The methyl group forms a bond to the aldehyde carbonyl carbon, and the resulting alkoxide oxygen is protonated during work-up. Addition to either face of the planar carbonyl group gives the two enantiomers in equal amounts under achiral conditions.

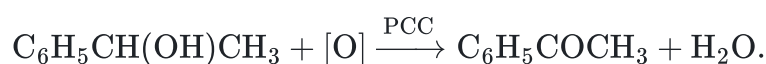
Label	Approximate δ / ppm	Assignment	Multiplicity
E1	7.3	Five aromatic H	Aromatic envelope
E2	4.8	CH(OH), 1 H	Quartet
E3	2.2	Hydroxyl H, 1 H	Exchangeable singlet
E4	1.5	CH ₃ , 3 H	Doublet

The methine proton couples to the three methyl protons, while the methyl protons couple to the methine proton. The acid-catalysed exchange mentioned in the problem explains why the hydroxyl proton does not produce resolved additional splitting. Its shift and linewidth depend on the exchange conditions.

F — Alcohol oxidation and closure of the reaction cycle

Pyridinium chlorochromate (PCC), SMILES c1cc[nH+]cc1.[O-][Cr](=O)=OCl, oxidizes the secondary alcohol E to the ketone **acetophenone**, **F**.

Using [O] to denote one oxygen-atom equivalent supplied by the oxidant, the balanced organic transformation is



Label	Approximate δ / ppm	Assignment	Multiplicity
F1	7.4–8.0	Five aromatic H	Multiplets
F2	2.6	COCH ₃ , 3 H	Singlet

The methyl group has no adjacent proton-bearing carbon, so its signal is a singlet. Its downfield position is consistent with attachment to a carbonyl group. The methine and hydroxyl resonances of E disappear.

Finally, **hydrazine**, SMILES NN, with **sodium hydroxide**, SMILES [Na+].[OH-], effects a Wolff–Kishner reduction on heating:



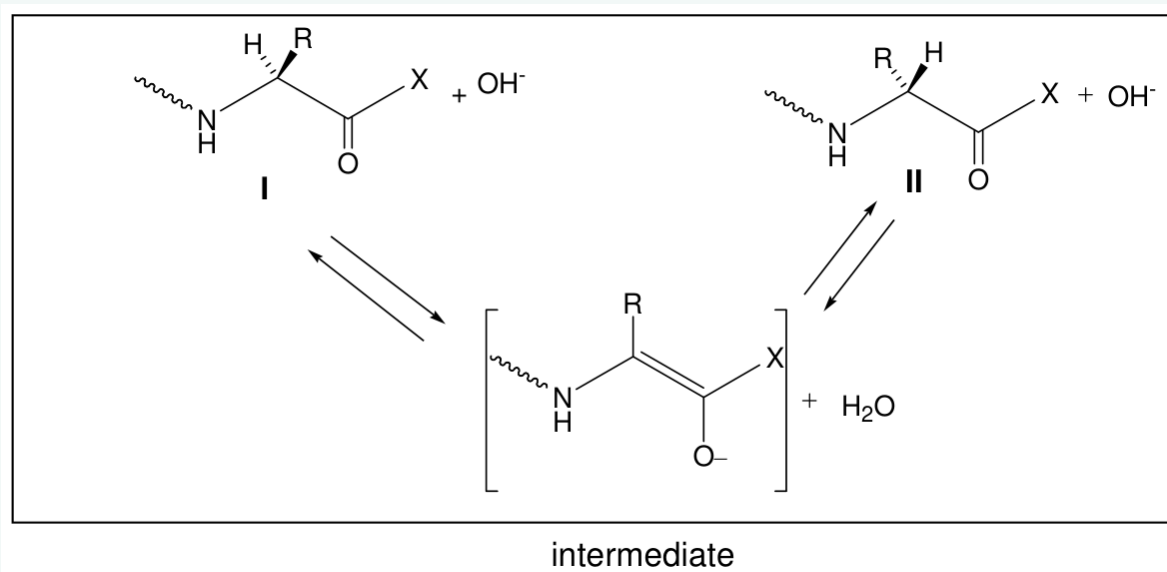
The carbonyl group becomes a methylene group, regenerating **ethylbenzene**, **A**. The byproducts are **dinitrogen**, SMILES N#N, and **water**, SMILES O.

For completeness, the other species in the balanced work-up equations are **ozone** $O=[O^+][O^-]$, **zinc** $[Zn]$, **hydronium** $[OH_3^+]$, **zinc(II) ion** $[Zn^{2+}]$, **magnesium(II) ion** $[Mg^{2+}]$, and **bromide ion** $[Br^-]$.

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 33: Peptides

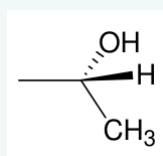
Racemization of α -aminoacids and peptides can occur by an α -enolization mechanism and both heat and the presence of strong bases greatly accelerate the process:



1. Draw stereochemical formulas **I** and **II** (with bold and dashed bonds) for the aminoacid components of the mixture that has reached equilibrium through the α -enolization mechanism described above operating on each of the following hydroxyaminoacids **A** and **B**:

A: serine ($R = -CH_2OH$)

B: (2*S*, 3*R*)-threonine ($R =$

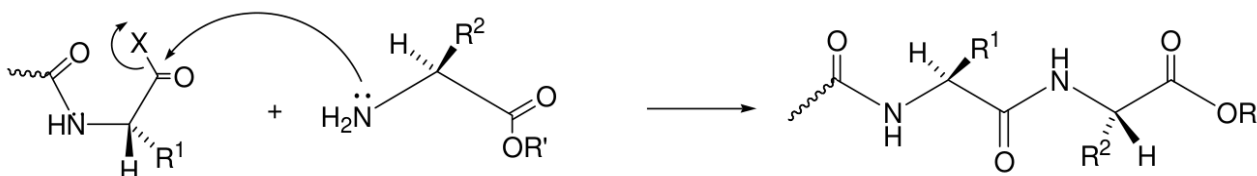


)

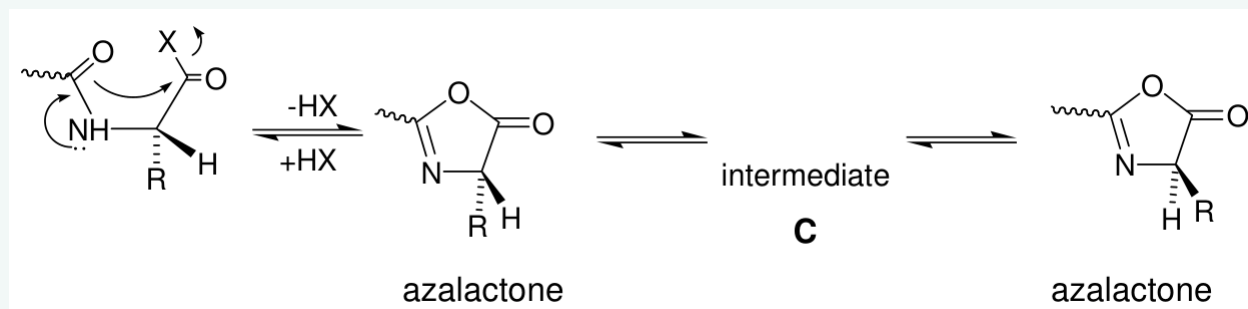
2. Mark the box that corresponds to the correct definition of the relationship between the structures you have drawn in each of the above cases A and B.

	enantiomers	diastereomers
A _{I,II}	☐	☐
B _{I,II}	☐	☐

During peptide synthesis, in order to form a new peptide bond the carboxyl group has to be activated, that is, it must bear a good leaving group, represented in a simplified scheme below:



It is at this stage of the synthesis that a second racemization mechanism may occur; the amidic carbonyl oxygen is five atoms away from the activated carboxyl group and can intramolecularly attack the activated carboxyl forming a five membered cyclic intermediate (an azalactone) which quickly equilibrates its hydrogen at the stereogenic center, represented in a simplified scheme below:



3. Write the structural formula for the intermediate **C** that interconverts the two azalactones and thus explains the scrambling of the stereochemistry at the stereogenic center.

Azalactones are very reactive substances that can still react with the amino group of an amino acid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

4. If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to $40\text{ }^{\circ}\text{C}$ with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$ (**P₁**).

a) Propose a structure for substance **P₁**.

b) Write the reaction product(s) of the substance **P₁** with *S*-alanine ethyl ester (**P₂**) (the side chain R of the amino acid alanine is a methyl group) using stereochemical formulas (with bold and dashed bonds) for both reactants and product.

Official English text of the problem.

Answers

1. **A — serine:** - **I:** $(2S)$ -serine, $N[C@@H](CO)C(=O)O$. - **II:** $(2R)$ -serine, $N[C@H](CO)C(=O)O$.

B — threonine: - **I:** $(2S, 3R)$ -threonine, $N[C@@H](C[C@H](O)C)C(=O)O$. - **II:** $(2R, 3R)$ -allo-threonine, $N[C@H](C[C@H](O)C)C(=O)O$.

Precise wedge-and-dash drawing instructions are given below.

2. **A:** enantiomers. **B:** diastereomers, specifically epimers at C2.

3. **C:** the planar enol tautomer, a **2,4-disubstituted-1,3-oxazol-5-ol**, *C1=NC(*)=C(O)O1.

The first * represents the substituent from the N-acyl group; the second represents the aminoacid side chain R.

4. **(a) P₁: 2-phenyl-1,3-oxazol-5(4H)-one**, the glycine-derived azlactone,

O=C1CN=C(c2ccccc2)O1.

(b) P₂: ethyl (2*S*)-2-aminopropanoate, N[C@@H](C)C(=O)OCC.

The single coupling product is **N-benzoylglycyl-(*S*)-alanine ethyl ester**,

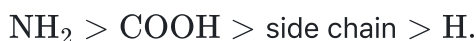
O=C(c1ccccc1)NCC(=O)N[C@@H](C)C(=O)OCC. Its alanine stereocenter remains *S*.

Solution

1. Stereochemical products of α-enolization

Removal of the α-hydrogen gives an intermediate whose α-carbon is trigonal planar. Reprotonation from either face restores a tetrahedral carbon and produces either configuration at that carbon.

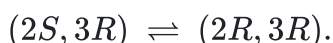
For both aminoacids, the priority order at C2 is



The carboxyl carbon outranks the side-chain carbon because its attached-atom list, counting the carbonyl double bond according to the CIP rules, is (O, O, O). The corresponding lists for the serine and threonine side chains are (O, H, H) and (O, C, H), respectively.

A: serine. Serine has only one stereogenic center. Enolization therefore interconverts (2*S*)-serine and (2*R*)-serine. In an achiral medium, their equilibrium mixture is racemic.

B: threonine. The stated mechanism removes the hydrogen at C2. It does not change the configuration of the side-chain carbon C3. Consequently,



The second component is (2*R*, 3*R*)-allo-threonine. The two components need not occur in a 1 : 1 equilibrium ratio because they are diastereomers.

For the requested drawings, use the following precise convention. Ordinary bonds lie in the page; a solid wedge points toward the viewer, and a dashed wedge points away.

- At C2, draw the bond to the carboxyl carbon down-left and the bond to the side chain down-right, both in the page.
- For **I**, draw NH₂ up-right on a solid wedge and H up-left on a dashed wedge. This gives 2*S*.
- For **II**, draw NH₂ up-left on a dashed wedge and H up-right on a solid wedge. This gives 2*R*.
- For threonine, continue the drawing at C3 with its bond to C2 up-left and its bond to CH₃ up-right, both in the page. Draw OH down-right on a solid wedge and H down-left on a dashed wedge. Keep this arrangement in both **B-I** and **B-II**: it gives 3*R*.

These structures are written in the neutral aminoacid form; protonation state does not alter the stereochemical conclusions.

2. Relationships between the products

For serine, inversion of its only stereogenic center produces its nonsuperimposable mirror image. The pair consists of **enantiomers**.

For threonine, C2 is inverted while C3 retains its configuration. The products are therefore **diastereomers**, specifically **C2 epimers**.

The completed boxes are:

	enantiomers	diastereomers
A_{I,II}	☒	☐
B_{I,II}	☐	☒

3. Intermediate C

Number the azlactone ring consecutively as O1–C2–N3–C4–C5. The aminoacid α -carbon becomes ring carbon C4.

Enolization transfers the C4 hydrogen to the carbonyl oxygen, changing the C4–C5 bond into a double bond and the C5 carbonyl into an hydroxyl group. The resulting neutral intermediate is the **2,4-disubstituted-1,3-oxazol-5-ol** identified above:



To draw it, construct a five-membered ring with these successive bonds and substituents:

- O1–C2, with the original N-acyl substituent attached to C2;
- C2=N3;
- N3–C4, with side chain R attached to C4;
- C4=C5, with OH attached to C5;
- C5–O1, closing the ring.

C4 has no hydrogen in this tautomer and is planar, so it has no wedge or dashed bond specifying a configuration. On returning to the carbonyl form, protonation at C4 can occur from either face.

Under basic conditions, the corresponding **azlactone enolate**, $*C1=NC(*)=C([O-])O1$, provides the same loss of configuration at C4. Its negative charge is delocalized; the displayed SMILES gives the oxygen-charged resonance form.

4(a). Identification and formation of P₁

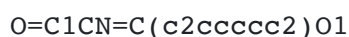
The starting material is **N-benzoylglycine (hippuric acid)**, $O=C(O)CNC(=O)c1ccccc1$.

The formula change



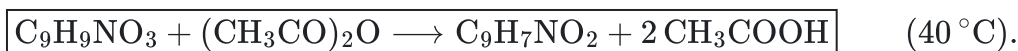
corresponds formally to loss of one molecule of **water**, H_2O . This is consistent with cyclodehydration to an azlactone.

Acetic anhydride, $CC(=O)OC(=O)C$, activates the carboxyl group. The benzamide carbonyl oxygen attacks the activated carboxyl carbon intramolecularly. Elimination and proton transfer then form **2-phenyl-1,3-oxazol-5(4H)-one**, P_1 :



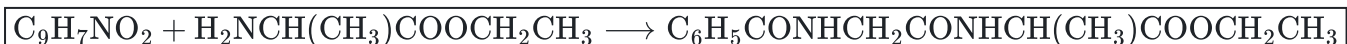
For its drawing, the five-membered ring has the successive atoms and bonds O1–C2=N3–C4–C5–O1. Attach a phenyl group to C2, draw C4 as CH₂, and draw a carbonyl oxygen double-bonded to C5. There is no stereogenic center in P_1 .

With acetic anhydride included, the balanced overall reaction produces **acetic acid**, CC(=O)O:

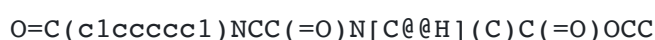


4(b). Reaction with S-alanine ethyl ester

The amino nitrogen of **ethyl (2*S*)-2-aminopropanoate**, P_2 , attacks the C5 carbonyl of P_1 . Collapse of the tetrahedral intermediate breaks the C5–O1 ring bond. Proton transfers restore the benzamide carbonyl and give the peptide:



The product is **N-benzoylglycyl-(*S*)-alanine ethyl ester**:



All atoms of the two reactants are retained. The molecular-formula balance is



For the stereochemical drawings of P_2 and the product, place the alanine α-carbon's bond to the ester carbonyl down-left and its bond to CH₃ down-right, both in the page. Draw its bond to nitrogen up-right on a solid wedge and its bond to hydrogen up-left on a dashed wedge. This gives *S* in both structures. The nitrogen bears two hydrogens in P_2 ; in the product, it bears one hydrogen and the acyl group –C(=O)CH₂NHC(=O)C₆H₅.

The glycine residue remains CH₂ and cannot become a stereogenic center. The alanine stereocenter is retained during coupling. Thus the specified azlactone pathway gives **one stereochemical product**.

The solution was checked against the official solution.

Problem 34: Aluminium

SECTION D: Inorganic Chemistry

PROBLEM 34 Aluminium

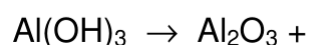
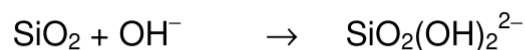
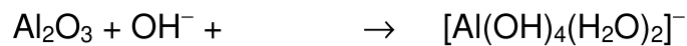
One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina (Al₂O₃) and aluminium metal using the mineral bauxite mined from the Parnassus mountain.

Bauxite is a mixed aluminium oxide hydroxide – AlO_{*x*}(OH)_{3–2*x*} where 0 < *x* < 1.

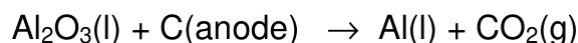
Production of Al metal follows a two-stage process:

(i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are Al₂O₃ 40 – 60 %, H₂O 12 – 30 %, SiO₂ free and combined 1 – 15 %, Fe₂O₃ 7 – 30 %, TiO₂ 3 – 4 %, F, P₂O₅, V₂O₅, etc., 0.05 – 0.2 %). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200 °C.

Complete and balance the following chemical reactions:



ii) Hérault-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, Na_3AlF_6 . Typical electrolyte composition ranges are Na_3AlF_6 (80 – 85 %), CaF_2 (5 – 7 %), AlF_3 (5 – 7 %), Al_2O_3 (2 – 8 % intermittently recharged). Electrolysis is carried out at 940 °C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:



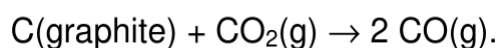
Since cryolite is a rather rare mineral, it is prepared according to the following reaction.

Complete and balance this reaction:



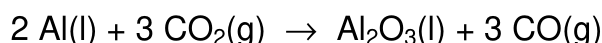
During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

iii) By using the thermodynamic data given below, which are taken to be independent on temperature, determine the thermodynamic quantities ΔH , ΔS and ΔG at 940 °C for the reaction:



	Al(s)	Al ₂ O ₃ (s)	C (graphite)	CO (g)	CO ₂ (g)	O ₂ (g)
$\Delta_f H^\circ$ (kJ mol ⁻¹)	0	-1676	0	-111	-394	
S° (J K ⁻¹ mol ⁻¹)	28	51	6	198	214	205
$\Delta_{\text{fus}} H$ (kJ mol ⁻¹)	11	109				

iv) At the same temperature and using the data from the table in part (iii) determine the quantities ΔH and ΔG for the reaction



given that $\Delta S = -126 \text{ J K}^{-1} \text{ mol}^{-1}$. (Show your calculations)

v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxylaluminate anion, $[\text{Al}(\text{OH})_4]^- (\text{aq})$. In both cases liberation of H_2 occurs. AlF_3 is made by treating Al_2O_3 with HF gas at 700°C , while the other trihalides, AlX_3 , are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.

vi) The AlCl_3 is a crystalline solid having a layer lattice with 6-coordinate $\text{Al}(\text{III})$, but at the melting point (192.4°C) the structure changes to a 4-coordinate molecular dimer, Al_2Cl_6 . The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar AlCl_3 molecules.

For the molecular dimer Al_2Cl_6 , in the gas phase, two different $\text{Al}-\text{Cl}$ distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding $\text{Al}-\text{Cl}$ distances.

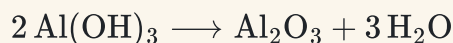
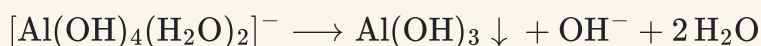
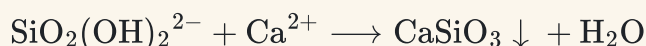
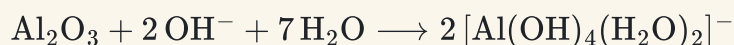
vii) What is the hybridization of the Al atom(s) in Al_2Cl_6 and AlCl_3 ?

Official English text of the problem.

Answers

Thermodynamic quantities below are per mole of reaction as written, at $T = 1213.15 \text{ K}$. Molecular and ionic names and SMILES are supplied in the corresponding solution parts.

- (i) The balanced reactions, with calcium silicate precipitation written in net ionic form, are:



- (ii) Electrolysis:



Cryolite preparation:



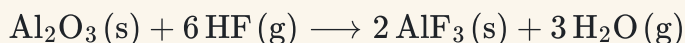
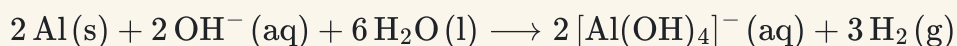
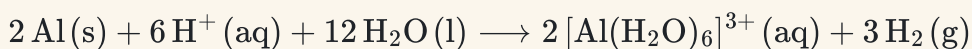
- (iii)

$$\Delta H = +172 \text{ kJ mol}^{-1}, \quad \Delta S = +176 \text{ J K}^{-1} \text{ mol}^{-1}, \quad \Delta G \approx -41.5 \text{ kJ mol}^{-1}$$

- (iv)

$$\Delta H = -740 \text{ kJ mol}^{-1}, \quad \Delta G \approx -587 \text{ kJ mol}^{-1}$$

- (v) The four reaction types are:



- (vi) Aluminium chloride dimer, Al_2Cl_6 , has two bridging and four terminal chlorine atoms. Each aluminium is approximately tetrahedral:

$$d(\text{Al}-\text{Cl}_{\text{terminal}}) = 206 \text{ pm}, \quad d(\text{Al}-\text{Cl}_{\text{bridging}}) = 221 \text{ pm}.$$

Dative-bond SMILES: Cl[Al](Cl)(Cl)Cl[Al](Cl)(Cl)Cl.

- (vii) In the conventional hybridization model:

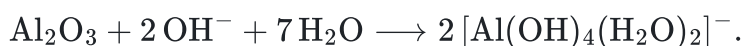
$$\text{Al}_2\text{Cl}_6 : \text{sp}^3 \text{ at each aluminium}; \quad \text{AlCl}_3 \text{ monomer} : \text{sp}^2.$$

Solution

Coordination compounds below use dative-bond SMILES, with donor-to-acceptor arrows. These specify connectivity; their spatial coordination geometries are described separately. Extended solids, including alumina, silica, aluminium hydroxide, calcium silicate, solid aluminium fluoride, graphite and metallic aluminium, do not have a single molecular SMILES.

(i) Bayer process

Alumina is amphoteric: it dissolves in hydroxide solution to form the soluble aluminate complex. Two aluminium atoms require two product anions, so charge balance requires two hydroxide ions. Oxygen and hydrogen balance then require seven water molecules:

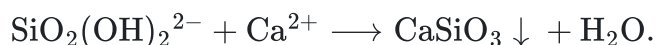


There are 12 oxygen atoms, 16 hydrogen atoms and total charge -2 on each side.

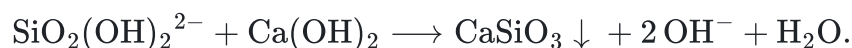
Silica is an acidic oxide. Addition of two hydroxide ions gives the specified doubly charged silicate:



Calcium ions remove this dissolved silicate by precipitation:

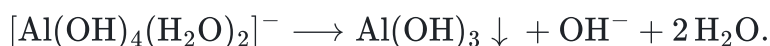


If calcium is supplied as calcium hydroxide, the equivalent reagent equation is



Thus lime addition also regenerates hydroxide.

Partial precipitation of aluminium hydroxide releases one hydroxide ion and the two coordinated water molecules:



Finally, heating dehydrates the hydroxide:



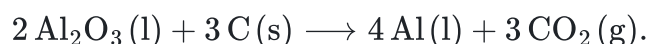
The relevant molecular and ionic identifiers are:

Species	Name	SMILES
H ₂ O	Water	O
OH ⁻	Hydroxide ion	[OH-]
[Al(OH) ₄ (H ₂ O) ₂] ⁻	Diaquatetrahydroxidoaluminate(III) ion	[Al+3](<-[OH-])(<-[OH-])(<-[OH-])(<-[OH-])(<-[OH2])<-[OH2]
SiO ₂ (OH) ₂ ²⁻	Dihydrogen orthosilicate ion	[O-][Si]([O-])(O)O
Ca ²⁺	Calcium(II) ion	[Ca+2]

The hydrated aluminate has six oxygen donors around aluminium, corresponding to octahedral coordination; the problem does not specify a cis/trans arrangement of the water ligands. The silicate has tetrahedral coordination around silicon. Calcium hydroxide has ionic formula-unit SMILES [Ca+2] . [OH-] . [OH-] .

(ii) Electrolysis and cryolite preparation

In electrolysis, each aluminium atom changes from oxidation state +3 to 0, accepting three electrons. Each carbon atom changes from 0 to +4 in carbon dioxide, releasing four electrons. The smallest common electron count is twelve, requiring four aluminium atoms and three carbon atoms:



This also balances all six oxygen atoms.

One formula unit of cryolite requires one aluminium, three sodium atoms and six fluorine atoms. Therefore the reactants must include one aluminium hydroxide, three sodium hydroxides and six hydrogen fluorides. Their remaining hydrogen and oxygen form six waters:

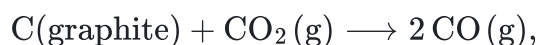


Hydrogen fluoride has SMILES F; carbon dioxide has SMILES O=C=O.

Cryolite is **sodium hexafluoroaluminate(III)**. Its ionic constituents are three sodium ions, [Na+], and one hexafluoroaluminate(III) ion, [AlF₆]³⁻, with dative-bond SMILES [Al+3](<-[F-])(<-[F-])(<-[F-])(<-[F-])(<-[F-])<-[F-]. The six fluorine donors form an octahedral coordination sphere. Sodium hydroxide has ionic formula-unit SMILES [Na+] . [OH-] .

(iii) Reaction of graphite with carbon dioxide

For



the reaction enthalpy is the sum of product formation enthalpies minus that of the reactants:

$$\begin{aligned} \Delta H &= 2\Delta_f H^\circ(\text{CO}) - [\Delta_f H^\circ(\text{C}) + \Delta_f H^\circ(\text{CO}_2)] \\ &= 2(-111) - [0 + (-394)] \\ &= \boxed{+172 \text{ kJ mol}^{-1}}. \end{aligned}$$

Similarly,

$$\begin{aligned} \Delta S &= 2S^\circ(\text{CO}) - [S^\circ(\text{C}) + S^\circ(\text{CO}_2)] \\ &= 2(198) - (6 + 214) \\ &= \boxed{+176 \text{ J K}^{-1} \text{ mol}^{-1}}. \end{aligned}$$

The temperature is

$$T = 940 + 273.15 = 1213.15 \text{ K.}$$

Converting entropy to $\text{kJ K}^{-1} \text{ mol}^{-1}$,

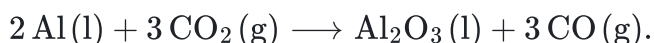
$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 172 - (1213.15)(0.176) \\ &= -41.5144 \text{ kJ mol}^{-1} \\ &\approx \boxed{-41.5 \text{ kJ mol}^{-1}}.\end{aligned}$$

The reaction is endothermic, but its positive entropy change—consistent with increasing the amount of gas from one to two moles—makes its standard Gibbs energy negative at this temperature. It therefore provides a thermodynamically favorable route for consuming the graphite anodes.

Carbon monoxide has SMILES [C-]#[O+]; carbon dioxide has SMILES O=C=O.

(iv) Oxidation of liquid aluminium by carbon dioxide

The reaction is



The formation enthalpies in the table refer to solid aluminium and solid alumina. Within the problem's temperature-independent approximation, the required liquid-state enthalpies are

$$\Delta_f H(\text{Al(l)}) = 0 + 11 = 11 \text{ kJ mol}^{-1},$$

and

$$\Delta_f H(\text{Al}_2\text{O}_3(\text{l})) = -1676 + 109 = -1567 \text{ kJ mol}^{-1}.$$

Consequently,

$$\begin{aligned}\Delta H &= [-1567 + 3(-111)] - [2(11) + 3(-394)] \\ &= -1900 - (-1160) \\ &= \boxed{-740 \text{ kJ mol}^{-1}}.\end{aligned}$$

Equivalently, the solid-state reaction enthalpy is -827 kJ mol^{-1} , and the net fusion correction is

$$109 - 2(11) = 87 \text{ kJ mol}^{-1},$$

giving $-827 + 87 = -740 \text{ kJ mol}^{-1}$.

Using the supplied reaction entropy,

$$\Delta S = -126 \text{ J K}^{-1} \text{ mol}^{-1} = -0.126 \text{ kJ K}^{-1} \text{ mol}^{-1},$$

we obtain

$$\begin{aligned}\Delta G &= -740 - (1213.15)(-0.126) \\ &= -587.1431 \text{ kJ mol}^{-1} \\ &\approx \boxed{-587 \text{ kJ mol}^{-1}}.\end{aligned}$$

This strongly favorable standard Gibbs energy explains how contact with carbon dioxide can reoxidize the aluminium product and lower its yield.

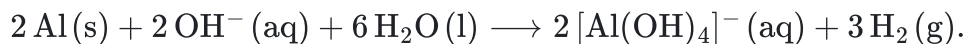
(v) Reactions of aluminium and preparation of its halides

In acid, two aluminium atoms lose six electrons in total, while six hydrogen ions are reduced to three hydrogen molecules. Twelve water molecules provide the six aqua ligands on each aluminium:



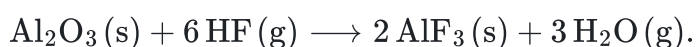
Chloride is a spectator ion in this net ionic equation.

In base, aluminium is again oxidized to +3, but the product is tetrahydroxidoaluminate:



Both sides contain two aluminium atoms, eight oxygen atoms, fourteen hydrogen atoms and total charge -2 .

Treatment of alumina with hydrogen fluoride at 700°C is an acid–base conversion with no change in aluminium's oxidation state:



Six hydrogen fluorides supply the six fluorines for two aluminium fluorides and the six hydrogens for three waters.

For chlorine, bromine and iodine, direct combination is a redox reaction:



Two aluminium atoms release six electrons, and the six halogen atoms each accept one.

Additional molecular and ionic identifiers are:

Species	Name	SMILES
HCl	Hydrogen chloride; its aqueous solution is hydrochloric acid	C1
H ⁺	Hydrogen ion, used as the aqueous acid notation	[H+]
Cl [−]	Chloride ion	[Cl-]
H ₂	Hydrogen	[H][H]
[Al(H ₂ O) ₆] ³⁺	Hexaaquaaluminium(III) ion	[Al+3](<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])(<-[OH2])
[Al(OH) ₄] [−]	Tetrahydroxidoaluminate(III) ion	[Al+3](<-[OH-])(<-[OH-])(<-[OH-])(<-[OH-])
Cl ₂	Chlorine	ClCl
Br ₂	Bromine	BrBr
I ₂	Iodine	II

Hexaaquaaluminium(III) is octahedral, whereas tetrahydroxidoaluminate(III) is tetrahedral. Aqueous hydrogen ions are solvated; [H+] is the conventional shorthand used in the net ionic equation.

The trihalide **monomer connectivities** are aluminium chloride C1[Al](Cl)Cl, aluminium bromide Br[Al](Br)Br and aluminium iodide I[Al](I)I. These strings alone do not specify aggregation into dimers or condensed-phase structures.

(vi) Structure and bond lengths of the dimer

An isolated aluminium chloride monomer has only six electrons in aluminium's valence shell. Dimerization allows one chlorine from each monomer to donate a lone pair to the other aluminium, forming two chlorine bridges. Each aluminium then has four chlorine neighbours: two terminal and two bridging.

The aluminium chloride dimer has dative-bond SMILES: Cl[Al](Cl)Cl[Al](Cl)Cl.

The requested stereostructure should be drawn as follows:

1. Place the two aluminium atoms at the left and right vertices of a diamond, with the two bridging chlorines at its upper and lower vertices. Join each bridging chlorine to both aluminium atoms. This gives a planar, four-membered central ring.
2. Attach two terminal chlorines to each aluminium, directed outward from the ring: one on a solid wedge toward the viewer and one on a dashed wedge away from the viewer.
3. Label all four terminal bonds **206 pm** and all four aluminium-to-bridging-chlorine bonds **221 pm**. There is no direct aluminium–aluminium bond.

This is two distorted coordination tetrahedra sharing the edge defined by the two bridging chlorines. The bridging contacts are longer than the terminal bonds because each bridging chlorine participates in bonding to two aluminium centres.

The donor arrows in the SMILES are a bonding-bookkeeping representation; they do not imply different lengths for the four symmetry-equivalent bridge contacts.

(vii) Hybridization

In the dimer, each aluminium has four approximately tetrahedrally arranged bonding directions. The conventional assignment is therefore



The gaseous aluminium chloride monomer, Cl[Al](Cl)Cl, has three coplanar bonds with approximately 120° bond angles. Its conventional assignment is



with an empty p orbital perpendicular to the molecular plane.

These assignments concern the molecular dimer and monomer described in part (vi), rather than the six-coordinate aluminium sites in the crystalline solid.

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 35: Kinetics

The acid-catalyzed reaction $\text{CH}_3\text{COCH}_3 + \text{I}_2 \longrightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$ was found to be of first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by $0.010 \text{ mol dm}^{-3}$ was measured under various concentrations of the reactants.

Based on the information provided in the table, answer fulfil the following tasks:

$[\text{CH}_3\text{COCH}_3]$	$[\text{I}_2]$	Time
(mol dm^{-3})	(mol dm^{-3})	(min)
0.25	0.050	7.2
0.50	0.050	3.6
1.00	0.050	1.8
0.50	0.100	3.6
0.25	0.100	...
1.50	...	...
...	...	0.36

- Derive the rate law for the reaction and calculate the rate constant.
- Calculate the time needed for 75 % of CH_3COCH_3 to react in excess I_2 .
- Show graphically the dependence of the rate on $[\text{CH}_3\text{COCH}_3]$ and on $[\text{I}_2]$, for fixed initial concentration of the other reagents.
- If the rate is doubled by raising the temperature by 10 °C from 298 K, calculate the activation energy for this reaction.

Official English text of the problem.

Answers

- a)** The rate law is

$$v = k[\text{H}^+][\text{CH}_3\text{COCH}_3].$$

At the fixed hydrogen-ion concentration,

$$k_{\text{obs}} \equiv k[\text{H}^+] \simeq 5.6 \times 10^{-3} \text{ min}^{-1}.$$

The full constant k cannot be evaluated numerically without $[\text{H}^+]$. The missing times are **7.2 min** and **1.2 min**; the missing acetone concentration is 5.0 mol dm^{-3} . The missing iodine concentrations are not uniquely determined.

- b)** At the same constant hydrogen-ion concentration,

$$t_{75\%} \simeq 2.5 \times 10^2 \text{ min} \simeq 4.2 \text{ h}.$$

- c)** Rate versus acetone concentration: **a straight line through the origin**, with slope k_{obs} .
Rate versus iodine concentration: **a horizontal line** over the range where the zero-order iodine dependence applies.
- d)**

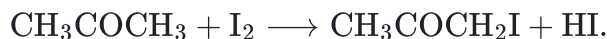
$$E_{\text{a}} \simeq 53 \text{ kJ mol}^{-1}.$$

Solution

a) Rate law and rate constant

The species are acetone (propan-2-one), CH_3COCH_3 ; molecular iodine, I_2 ; iodoacetone (1-iodopropan-2-one), $\text{CH}_3\text{COCH}_2\text{I}$; hydrogen iodide, HI ; and the hydrogen-ion catalyst, $[\text{H}^+]$.

The balanced reaction is



Its 1 : 1 stoichiometry gives

$$v = -\frac{d[\text{I}_2]}{dt} = -\frac{d[\text{CH}_3\text{COCH}_3]}{dt}.$$

Since first-order dependence on hydrogen ions is given, write

$$v = k[\text{H}^+][\text{CH}_3\text{COCH}_3]^m[\text{I}_2]^n.$$

Each measurement corresponds to the same iodine concentration decrease, so the average rate is

$$\bar{v} = \frac{0.010 \text{ mol dm}^{-3}}{t}.$$

The acetone concentration changes by only 1–4% in the first four experiments, so these average rates approximate the initial rates.

At fixed iodine concentration, doubling the acetone concentration halves the time:

$$\frac{v_2}{v_1} = \frac{7.2}{3.6} = 2 = \left(\frac{0.50}{0.25}\right)^m.$$

Thus $m = 1$, also confirmed by the next doubling from 0.50 to 1.00 mol dm^{-3} .

At fixed acetone concentration, doubling the iodine concentration leaves the time unchanged:

$$\frac{v_4}{v_2} = \frac{3.6}{3.6} = 1 = \left(\frac{0.100}{0.050}\right)^n.$$

Thus $n = 0$.

Therefore,

$$v = k[\text{H}^+][\text{CH}_3\text{COCH}_3].$$

The reaction is first order in acetone, first order in hydrogen ions, and zero order in iodine: second order overall.

At constant hydrogen-ion concentration, define

$$k_{\text{obs}} = k[\text{H}^+], \quad v = k_{\text{obs}}[\text{CH}_3\text{COCH}_3].$$

Using the second experiment,

$$k_{\text{obs}} \simeq \frac{0.010 \text{ mol dm}^{-3}}{(3.6 \text{ min})(0.50 \text{ mol dm}^{-3})} = 5.56 \times 10^{-3} \text{ min}^{-1}.$$

The full rate constant is

$$k = \frac{k_{\text{obs}}}{[\text{H}^+]},$$

with units $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$. Its numerical value requires the hydrogen-ion concentration.

Under the same short-interval approximation,

$$[\text{CH}_3\text{COCH}_3] t = \frac{0.010 \text{ mol dm}^{-3}}{k_{\text{obs}}} = 1.8 \text{ mol dm}^{-3} \text{ min}.$$

Hence the incomplete rows become:

$[\text{CH}_3\text{COCH}_3] / \text{mol dm}^{-3}$	$[\text{I}_2] / \text{mol dm}^{-3}$	Time / min
0.25	0.100	7.2
1.50	Not determined	1.2
5.0	Not determined	0.36

The unspecified iodine concentrations must permit the stated concentration decrease and lie within the regime of zero-order iodine dependence.

b) Time for 75% conversion

With iodine in excess and hydrogen-ion concentration held constant,

$$-\frac{d[\text{CH}_3\text{COCH}_3]}{dt} = k_{\text{obs}}[\text{CH}_3\text{COCH}_3].$$

Integration gives

$$\ln\left(\frac{[\text{CH}_3\text{COCH}_3]_0}{[\text{CH}_3\text{COCH}_3]_t}\right) = k_{\text{obs}}t.$$

After 75% has reacted, 25% remains:

$$[\text{CH}_3\text{COCH}_3]_t = 0.25[\text{CH}_3\text{COCH}_3]_0.$$

Therefore,

$$t_{75\%} = \frac{\ln 4}{k_{\text{obs}}} = \frac{1.3863}{5.5556 \times 10^{-3} \text{ min}^{-1}} = 249.5 \text{ min}.$$

Thus

$t_{75\%} \simeq 250 \text{ min} \simeq 4.2 \text{ h}.$

c) Dependence of rate on reactant concentrations

For both plots, put concentration in mol dm^{-3} on the horizontal axis and rate in $\text{mol dm}^{-3} \text{min}^{-1}$ on the vertical axis.

- **Rate against acetone concentration:** keeping hydrogen-ion and iodine concentrations fixed,

$$v = k_{\text{obs}}[\text{CH}_3\text{COCH}_3].$$

Draw a straight line through the origin with slope $5.6 \times 10^{-3} \text{ min}^{-1}$. Representative points are

$$(0.25, 1.39 \times 10^{-3}), \quad (0.50, 2.78 \times 10^{-3}), \quad (1.00, 5.56 \times 10^{-3}).$$

- **Rate against iodine concentration:** keeping hydrogen-ion and acetone concentrations fixed,

$$v = k_{\text{obs}}[\text{CH}_3\text{COCH}_3]_{\text{fixed}}.$$

Draw a horizontal line. For example, at an acetone concentration of 0.50 mol dm^{-3} , its height is $2.78 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$, including at iodine concentrations 0.050 and $0.100 \text{ mol dm}^{-3}$. This relation does not apply after iodine is exhausted.

d) Activation energy

At unchanged reactant concentrations, doubling the rate means doubling the rate constant. The temperatures are

$$T_1 = 298 \text{ K}, \quad T_2 = 308 \text{ K}.$$

The Arrhenius relation gives

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

Using $k_2/k_1 = 2$ and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$E_a = \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln 2}{(1/298 - 1/308) \text{ K}^{-1}} = 5.289 \times 10^4 \text{ J mol}^{-1}.$$

Therefore,

$$\boxed{E_a \simeq 53 \text{ kJ mol}^{-1}}.$$

The solution was checked against the official solution.