

IChO 1994

Theory problems and solutions · Oslo, Norway · 8 theory problems with complete solutions

eulersolve.org/icho/1994/

Problem 1: Lactic acid, hydrogen carbonate and calcium in blood

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. This will be illustrated by the following calculations:

Lactic acid written as HL is monoprotic, and the acid dissociation constant is $K_{\text{HL}} = 1.4 \times 10^{-4}$.

The acid dissociation constants for carbonic acid are: $K_{a1} = 4.5 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$. All carbon dioxide remains dissolved during the reactions.

1.1 Calculate pH in a 3.00×10^{-3} M solution of HL.

1.2 Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate.

1.3 3.00×10^{-3} mol of lactic acid (HL) is added to 1.00 dm^3 of 0.024 M solution of NaHCO_3 (no change in volume, HL completely neutralized).

i) Calculate the value of pH in the solution of NaHCO_3 before HL is added.

ii) Calculate the value of pH in the solution after the addition of HL.

1.4 pH in the blood of a person changed from 7.40 to 7.00 due to lactic acid formed during physical activity. Let an aqueous solution having $pH = 7.40$ and $[\text{HCO}_3^-] = 0.022$ represent blood in the following calculation. How many moles of lactic acid have been added to 1.00 dm^3 of this solution when its pH has become 7.00?

1.5 In a saturated aqueous solution of CaCO_3 (s) pH is measured to be 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant K_{sp} is 5×10^{-9} .

1.6 Blood contains calcium. Determine the maximum concentration of "free" calcium ions in the solution ($pH = 7.40$, $[\text{HCO}_3^-] = 0.022$) given in 1.4.

Official English text of the problem.

Answers

- **1.1:** $pH = 3.24$.
- **1.2:** $\text{HL} + \text{HCO}_3^- \rightleftharpoons \text{L}^- + \text{H}_2\text{CO}_3$, with $K = 3.1 \times 10^2$.
- **1.3(i):** $pH = 8.34$.

- **1.3(ii):** $\text{pH} = 7.19$.
- **1.4:** $n(\text{HL}) = 2.4 \times 10^{-3} \text{ mol}$.
- **1.5:** $s = 1.3 \times 10^{-4} \text{ mol dm}^{-3}$; $K_{sp} \approx 4.7 \times 10^{-9}$, which rounds to 5×10^{-9} .
- **1.6:** $[\text{Ca}^{2+}]_{\text{max}} \approx 2 \times 10^{-4} \text{ mol dm}^{-3}$ (1.93×10^{-4} before rounding).

Solution

We use dilute-solution concentration equilibria and, where required, $K_w = 1.0 \times 10^{-14}$. Write $h = [\text{H}_3\text{O}^+]$. For the carbonate calculations, $[\text{H}_2\text{CO}_3]$ denotes the undissociated carbonic-acid component represented by the supplied K_{a1} , conventionally including dissolved carbon dioxide.

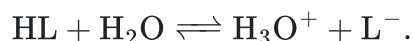
The chemical species and their SMILES are:

Name and notation	SMILES
Lactic acid, HL	<chem>CC(O)C(=O)O</chem>
Lactate ion, L^-	<chem>CC(O)C(=O)[O-]</chem>
Carbonic acid, H_2CO_3	<chem>O=C(O)O</chem>
Carbon dioxide, CO_2	<chem>O=C=O</chem>
Hydrogen carbonate ion, HCO_3^-	<chem>O=C(O)[O-]</chem>
Carbonate ion, CO_3^{2-}	<chem>O=C([O-])[O-]</chem>
Water, H_2O	<chem>O</chem>
Hydronium ion, H_3O^+	<chem>[OH3+]</chem>
Hydroxide ion, OH^-	<chem>[OH-]</chem>
Calcium ion, Ca^{2+}	<chem>[Ca+2]</chem>
Sodium hydrogen carbonate, NaHCO_3	<chem>[Na+].O=C(O)[O-]</chem>
Calcium carbonate, CaCO_3	<chem>[Ca+2].O=C([O-])[O-]</chem>

Lactic-acid stereochemistry does not affect these equilibria and is left unspecified. The disconnected salt SMILES describe ionic composition; they do not encode a crystal lattice.

1.1 — pH of lactic acid

The dissociation is



For initial concentration $C = 3.00 \times 10^{-3} \text{ M}$, let x dissociate. Neglecting water autoionization,

$$[\text{H}_3\text{O}^+] = [\text{L}^-] = x, \quad [\text{HL}] = C - x.$$

Therefore,

$$K_{\text{HL}} = \frac{x^2}{C - x},$$

and the positive quadratic root is

$$x = \frac{-K_{\text{HL}} + \sqrt{K_{\text{HL}}^2 + 4K_{\text{HL}}C}}{2} = 5.8184 \times 10^{-4} \text{ M}.$$

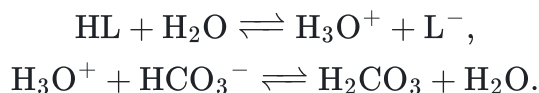
Thus

$$\boxed{\text{pH} = 3.24}.$$

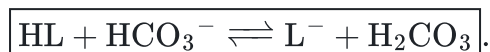
About 19.4% of the acid dissociates, so the approximation $C - x \approx C$ would not be sufficiently accurate here.

1.2 — Equilibrium constant for neutralization

Add lactic-acid dissociation to the reverse of the first carbonic-acid dissociation:



The balanced overall reaction is



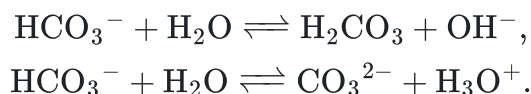
Its equilibrium constant is

$$K = \frac{[\text{L}^-][\text{H}_2\text{CO}_3]}{[\text{HL}][\text{HCO}_3^-]} = \frac{K_{\text{HL}}}{K_{a1}} = \frac{1.4 \times 10^{-4}}{4.5 \times 10^{-7}} = \boxed{3.1 \times 10^2}.$$

The reaction therefore strongly favors proton transfer from lactic acid to hydrogen carbonate.

1.3(i) — pH before adding lactic acid

Hydrogen carbonate is amphiprotic. It can accept or donate a proton:



For a solution of the hydrogen carbonate salt, neglecting the small contribution of water autoionization, mass balance and electroneutrality give

$$[\text{H}_2\text{CO}_3] \approx [\text{CO}_3^{2-}].$$

The two acid-dissociation expressions give

$$K_{a1}K_{a2} = \left(\frac{h[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right) \left(\frac{h[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right) \approx h^2.$$

Hence

$$\text{pH} = \frac{1}{2}(pK_{a1} + pK_{a2}) = \frac{1}{2}(6.3468 + 10.3279) = \boxed{8.34}.$$

1.3(ii) — pH after adding lactic acid

According to the stated complete-neutralization assumption, each mole of lactic acid converts one mole of hydrogen carbonate into carbonic acid:



The original amount of hydrogen carbonate is

$$n_0 = (0.024 \text{ mol dm}^{-3})(1.00 \text{ dm}^3) = 0.024 \text{ mol}.$$

After adding 0.00300 mol of lactic acid, the dominant carbonate-system concentrations are

$$\begin{aligned}[\text{HCO}_3^-] &\approx 0.024 - 0.00300 = 0.021 \text{ M}, \\ [\text{H}_2\text{CO}_3] &\approx 0.00300 \text{ M}.\end{aligned}$$

Using the first carbonic-acid equilibrium,

$$\text{pH} = \text{p}K_{a1} + \log_{10} \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]},$$

so

$$\text{pH} = 6.3468 + \log_{10} \frac{0.021}{0.00300} = 7.1919.$$

Therefore,

$$\boxed{\text{pH} = 7.19}.$$

The small carbonate contribution does not change this rounded result.

1.4 — Lactic acid required to lower pH from 7.40 to 7.00

Initially,

$$h_i = 10^{-7.40} = 3.9811 \times 10^{-8} \text{ M}.$$

The initial carbonic-acid concentration follows from K_{a1} :

$$[\text{H}_2\text{CO}_3]_i = \frac{h_i[\text{HCO}_3^-]_i}{K_{a1}} = \frac{(3.9811 \times 10^{-8})(0.022)}{4.5 \times 10^{-7}} = 1.9463 \times 10^{-3} \text{ M}.$$

At these pH values, lactic acid is essentially completely dissociated. For example, at the final pH,

$$\frac{[\text{L}^-]}{[\text{HL}]} = \frac{K_{\text{HL}}}{10^{-7.00}} = 1.4 \times 10^3.$$

The carbonate fraction is also small, since

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{K_{a2}}{h} \leq 1.2 \times 10^{-3}.$$

Neglecting that small fraction, let $x \text{ mol dm}^{-3}$ of added lactic acid react. Because carbon dioxide remains dissolved,

$$\begin{aligned} [\text{HCO}_3^-]_f &= 0.022 - x, \\ [\text{H}_2\text{CO}_3]_f &= 0.0019463 + x. \end{aligned}$$

At pH = 7.00,

$$\frac{[\text{HCO}_3^-]_f}{[\text{H}_2\text{CO}_3]_f} = \frac{K_{a1}}{h_f} = \frac{4.5 \times 10^{-7}}{1.0 \times 10^{-7}} = 4.5.$$

Thus

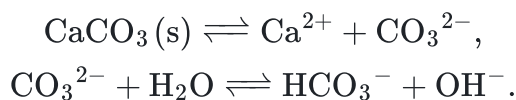
$$\begin{aligned} \frac{0.022 - x}{0.0019463 + x} &= 4.5, \\ x &= \frac{0.022 - 4.5(0.0019463)}{5.5} = 2.4076 \times 10^{-3} \text{ mol dm}^{-3}. \end{aligned}$$

For 1.00 dm^3 ,

$$\boxed{n(\text{HL}) = 2.4 \times 10^{-3} \text{ mol}}.$$

1.5 — Solubility and solubility product of calcium carbonate

Dissolution and carbonate hydrolysis occur:



Consequently, the dissolved carbonate is distributed among three acid–base forms.

At the measured pH,

$$\begin{aligned}h &= 10^{-9.95} = 1.1220 \times 10^{-10} \text{ M}, \\ [\text{OH}^-] &= \frac{K_w}{h} = 8.9125 \times 10^{-5} \text{ M}.\end{aligned}$$

Let

$$a = [\text{H}_2\text{CO}_3], \quad b = [\text{HCO}_3^-], \quad c = [\text{CO}_3^{2-}],$$

and let s be the molar solubility. For dissolution in pure water, the calcium and total inorganic-carbon concentrations are equal:

$$s = [\text{Ca}^{2+}] = a + b + c.$$

Electroneutrality requires

$$2s + h = b + 2c + [\text{OH}^-].$$

Substituting the carbon balance gives

$$2a + b = [\text{OH}^-] - h.$$

The acid equilibria give

$$a = \frac{h}{K_{a1}}b, \quad c = \frac{K_{a2}}{h}b.$$

Therefore,

$$\begin{aligned}b &= \frac{[\text{OH}^-] - h}{1 + 2h/K_{a1}} = 8.9081 \times 10^{-5} \text{ M}, \\ a &= \frac{h}{K_{a1}}b = 2.2211 \times 10^{-8} \text{ M}, \\ c &= \frac{K_{a2}}{h}b = 3.7315 \times 10^{-5} \text{ M}.\end{aligned}$$

The solubility is consequently

$$s = a + b + c = 1.2642 \times 10^{-4} \text{ mol dm}^{-3},$$

or

$$\boxed{s = 1.3 \times 10^{-4} \text{ mol dm}^{-3}}.$$

Finally,

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = (1.2642 \times 10^{-4})(3.7315 \times 10^{-5}) = 4.7172 \times 10^{-9}.$$

Thus, to the precision stated in the problem,

$$\boxed{K_{sp} \approx 5 \times 10^{-9}}.$$

1.6 — Maximum free calcium-ion concentration

At pH = 7.40, the second carbonic-acid equilibrium fixes the carbonate concentration:

$$[\text{CO}_3^{2-}] = \frac{K_{a2}[\text{HCO}_3^-]}{h} = \frac{(4.7 \times 10^{-11})(0.022)}{10^{-7.40}} = 2.5973 \times 10^{-5} \text{ M}.$$

The maximum equilibrium concentration of free calcium occurs at calcium-carbonate saturation:

$$[\text{Ca}^{2+}]_{\text{max}}[\text{CO}_3^{2-}] = K_{sp}.$$

Using the problem's rounded $K_{sp} = 5 \times 10^{-9}$,

$$[\text{Ca}^{2+}]_{\text{max}} = \frac{5 \times 10^{-9}}{2.5973 \times 10^{-5}} = 1.9251 \times 10^{-4} \text{ mol dm}^{-3}.$$

Therefore,

$$[\text{Ca}^{2+}]_{\text{max}} \approx 2 \times 10^{-4} \text{ mol dm}^{-3}.$$

The solution was checked against the official solution.

Problem 2: Kjeldahl determination of nitrogen

Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

2.1 0.2515 g of a grain sample was treated with sulphuric acid, sodium hydroxide was then added and the ammonia distilled into 50.00 cm³ of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 cm³ of 0.1050 M sodium hydroxide.

Calculate the concentration of nitrogen in the sample, in percent by mass.

2.2 Calculate the pH of the solution which is titrated in 2.1 when 0 cm³, 9.65 cm³, 19.30 cm³ and 28.95 cm³ of sodium hydroxide have been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid. K_a for ammonium ion is 5.7×10^{-10} .

2.3 Draw the titration curve based on the calculations in b).

2.4 What is the pH transition range of the indicator which could be used for the back titration.

2.5 The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occurring amino acid was determined by digesting 0.2345 g of the pure acid and distilling ammonia released into 50.00 cm³ of 0.1010 M hydrochloric acid. A titration volume of 17.50 cm³ was obtained for the back titration with 0.1050 M sodium hydroxide.

Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

Official English text of the problem.

Answers

- **2.1:** 16.84% nitrogen by mass.
- **2.2:** At added sodium hydroxide volumes 0, 9.65, 19.30, 28.95 cm³, respectively:
$$\text{pH} = 1.39, \quad 1.77, \quad 5.30, \quad 8.95.$$
- **2.3:** A smooth, increasing pH–volume curve through these four points, rising sharply around 19.30 cm³, then becoming less steep in the ammonium–ammonia buffer region.
- **2.4:** A transition interval approximately $\text{pH } 4\text{--}6$, encompassing the endpoint at pH 5.30, is suitable.
- **2.5:** The molar masses are 73.00 g mol^{-1} for one nitrogen atom per molecule and 146.0 g mol^{-1} for two. The corresponding relative molecular masses are 73.00 and 146.0.

Solution

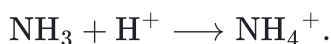
2.1 — Nitrogen content

The species involved in the ionic reactions are ammonium ion, NH_4^+ ([NH4+]); ammonia, NH_3 (N); hydroxide ion, OH^- ([OH-]); water, H_2O (O); and aqueous hydrogen ion, H^+ ([H+], representing a hydrated proton).

Digestion converts the nitrogen into ammonium ion. Addition of hydroxide releases ammonia:



The distilled ammonia consumes acid in a 1 : 1 molar ratio:



The remaining acid is determined by neutralization:



The initial amount of acid is

$$n_{\text{acid,initial}} = (0.05000 \text{ dm}^3)(0.1010 \text{ mol dm}^{-3}) = 5.050 \times 10^{-3} \text{ mol}.$$

The amount left after ammonia absorption equals the amount of back-titrant:

$$n_{\text{acid,remaining}} = (0.01930 \text{ dm}^3)(0.1050 \text{ mol dm}^{-3}) = 2.0265 \times 10^{-3} \text{ mol}.$$

Thus, retaining guard digits,

$$n_{\text{N}} = n_{\text{ammonia}} = (5.050 - 2.0265) \times 10^{-3} = 3.0235 \times 10^{-3} \text{ mol}.$$

Using the nitrogen atomic molar mass 14.01 g mol^{-1} ,

$$m_{\text{N}} = (3.0235 \times 10^{-3})(14.01) = 0.0423592 \text{ g}.$$

Therefore,

$$w_{\text{N}} = \frac{0.0423592}{0.2515} \times 100\% = 16.84\%.$$

2.2 — pH during the back titration

Before titration, the 50.00 cm^3 solution contains:

$$n_{\text{excess strong acid}} = 2.0265 \text{ mmol}, \quad n_{\text{ammonium}} = 3.0235 \text{ mmol}.$$

The strong acid dominates the pH before its neutralization. At 19.30 cm^3 , ammonium determines the pH. Subsequent hydroxide converts some ammonium into ammonia, forming a buffer.

At 0 cm^3

Ammonium dissociation is negligible in the presence of excess strong acid:

$$[\text{H}^+] = \frac{2.0265 \times 10^{-3} \text{ mol}}{0.05000 \text{ dm}^3} = 0.04053 \text{ mol dm}^{-3}.$$

Hence,

$$\boxed{\text{pH} = -\log_{10}(0.04053) = 1.39.}$$

At 9.65 cm^3

The added hydroxide neutralizes

$$n_{\text{hydroxide}} = (0.00965)(0.1050) = 1.01325 \times 10^{-3} \text{ mol}.$$

The remaining strong acid is therefore also $1.01325 \times 10^{-3} \text{ mol}$. Including dilution,

$$[\text{H}^+] = \frac{1.01325 \times 10^{-3}}{0.05000 + 0.00965} = 0.0169866 \text{ mol dm}^{-3},$$

so

$$\boxed{\text{pH} = 1.77.}$$

At 19.30 cm^3

The excess strong acid has been neutralized. Ammonium acts as a weak acid:



Its analytical concentration is

$$C = \frac{3.0235 \times 10^{-3}}{0.05000 + 0.01930} = 0.0436291 \text{ mol dm}^{-3}.$$

Writing $x = [\text{H}^+]$, the weak-acid equilibrium gives

$$K_a = \frac{x^2}{C - x}.$$

Because dissociation is small, $C - x \approx C$, and therefore

$$[\text{H}^+] \approx \sqrt{K_a C} = \sqrt{(5.7 \times 10^{-10})(0.0436291)} = 4.99 \times 10^{-6} \text{ mol dm}^{-3}.$$

Thus,

$$\boxed{\text{pH} = 5.30.}$$

The approximation is justified because $x/C \approx 1.1 \times 10^{-4}$.

At 28.95 cm^3

The hydroxide added beyond strong-acid neutralization reacts with ammonium:



The amount reacting in this stage is

$$n_{\text{hydroxide, additional}} = (0.02895 - 0.01930)(0.1050) = 1.01325 \times 10^{-3} \text{ mol}.$$

Consequently,

$$\begin{aligned} n_{\text{ammonia}} &= 1.01325 \text{ mmol}, \\ n_{\text{ammonium}} &= 3.02350 - 1.01325 = 2.01025 \text{ mmol}. \end{aligned}$$

Rearranging the ammonium acid-dissociation expression,

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{NH}_3]}{[\text{NH}_4^+]}.$$

Both species occupy the same volume, so their concentration ratio equals their mole ratio:

$$\begin{aligned} \text{pH} &= -\log_{10}(5.7 \times 10^{-10}) + \log_{10} \left(\frac{1.01325}{2.01025} \right) \\ &= 9.2441 - 0.2975. \end{aligned}$$

Therefore,

pH = 8.95.

2.3 — Description of the titration curve

Draw the horizontal axis as **volume of 0.1050 M sodium hydroxide added**, from 0 to approximately 30 cm³, and the vertical axis as **pH**, from approximately 0 to 10.

Mark these points:

Added volume / cm ³	pH
0.00	1.39
9.65	1.77
19.30	5.30
28.95	8.95

Draw a smooth curve that:

1. Begins at pH 1.39 and rises gradually through (9.65, 1.77).
2. Becomes increasingly steep as the excess strong acid approaches exhaustion.
3. Passes through the steep endpoint region at (19.30, 5.30).
4. Bends toward a gentler rise beyond the endpoint as the ammonium–ammonia buffer forms, reaching (28.95, 8.95).

Label 19.30 cm³ as the **excess strong-acid equivalence volume**.

2.4 — Indicator transition range

The indicator should change colour within the steep part of the curve surrounding the equivalence pH of 5.30. A transition interval approximately

pH 4–6

is suitable. This detects neutralization of the excess strong acid before an appreciable fraction of the ammonium has been converted into ammonia.

2.5 — Molecular weight of the amino acid

The amount of acid initially present is again

$$n_{\text{acid, initial}} = 5.050 \times 10^{-3} \text{ mol.}$$

The back titration measures the remaining acid:

$$n_{\text{acid, remaining}} = (0.01750)(0.1050) = 1.8375 \times 10^{-3} \text{ mol.}$$

Hence the amino-acid sample produces

$$n_{\text{ammonia}} = (5.050 - 1.8375) \times 10^{-3} = 3.2125 \times 10^{-3} \text{ mol.}$$

If each amino-acid molecule contains z nitrogen atoms, then

$$n_{\text{amino acid}} = \frac{n_{\text{ammonia}}}{z},$$

so its molar mass is

$$M = \frac{m}{n_{\text{amino acid}}} = \frac{zm}{n_{\text{ammonia}}}.$$

For **one nitrogen atom per molecule**,

$$M = \frac{0.2345 \text{ g}}{3.2125 \times 10^{-3} \text{ mol}} = 73.00 \text{ g mol}^{-1}.$$

For **two nitrogen atoms per molecule**,

$$M = \frac{2(0.2345 \text{ g})}{3.2125 \times 10^{-3} \text{ mol}} = 146.0 \text{ g mol}^{-1}.$$

The corresponding dimensionless relative molecular masses are 73.00 and 146.0, respectively.

The solution was checked against the official solution.

Problem 3: Sulphur oxohalides: structures and identification

Sulphur forms many different compounds with oxygen and halogens (sulphur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

3.1 Write Lewis structures for molecules SCl_2 , SO_3 , SO_2ClF , SF_4 , and SBrF_5 .

3.2 Carefully draw the geometries of the 5 molecules. (Disregard small deviations from "ideal" angles.)

3.3 A compound, consisting of sulphur (one atom per molecule), oxygen and one or more atoms of the elements F, Cl, Br, and I, was examined. A small amount of the substance reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1 M solutions of a series of test reagents were added to separate small portions of a diluted solution of the substance.

Which ions are being tested for in the following tests?

- i) Addition of HNO_3 and AgNO_3 .
- ii) Addition of $\text{Ba}(\text{NO}_3)_2$.
- iii) Adjustment to $\text{pH} = 7$ with NH_3 and addition of $\text{Ca}(\text{NO}_3)_2$.

Write the equations for the possible reactions in the tests:

- iv) Addition of KMnO_4 followed by $\text{Ba}(\text{NO}_3)_2$ to an acid solution of the substance.
- v) Addition of $\text{Cu}(\text{NO}_3)_2$.

3.4 In practice, the tests in 3.3 gave the following results:

- i) A yellowish precipitate.
- ii) No precipitate.
- iii) No visible reaction.
- iv) The main features were that the characteristic colour of permanganate disappeared, and a white precipitate was formed upon addition of $\text{Ba}(\text{NO}_3)_2$.
- v) No precipitate.

Write the formulas of the possible compounds, taking the results of these tests into account.

3.5 Finally, a simple quantitative analysis was undertaken:

7.190 g of the substance was weighed out and dissolved in water to give 250.0 cm^3 of a solution. To 25.00 cm^3 of this solution, nitric acid and enough AgNO_3 was added to secure complete precipitation. After washing and drying the precipitate weighed 1.452 g. Determine the formula of the compound.

3.6 Write the equation describing the reaction of the substance with water.

If you have not found the formula for the compound, use SOCIF.

Official English text of the problem.

Answers

• 3.1

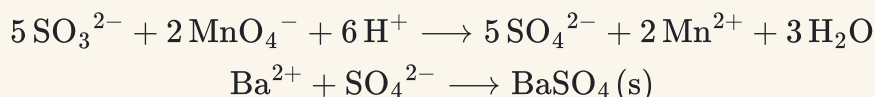
Molecule	SMILES	Bonds at sulphur	Lone pairs on sulphur
Sulphur dichloride, SCl_2	<chem>ClSCl</chem>	Two single bonds	2
Sulphur trioxide, SO_3	<chem>O=S(=O)=O</chem>	Three double bonds	0
Sulphuryl chloride fluoride, SO_2ClF	<chem>O=S(=O)(F)Cl</chem>	Two oxygen double bonds and two halogen single bonds	0
Sulphur tetrafluoride, SF_4	<chem>FS(F)(F)F</chem>	Four single bonds	1
Bromopentafluorosulphur, SBrF_5	<chem>FS(F)(F)(F)(F)Br</chem>	Six single bonds	0

Each terminal halogen has **three lone pairs**; each oxygen in these structures has **two lone pairs**. All formal charges are zero.

- **3.2** SCl_2 : bent; SO_3 : trigonal planar; SO_2ClF : tetrahedral; SF_4 : seesaw, with an equatorial lone pair; SBrF_5 : octahedral.

- **3.3**

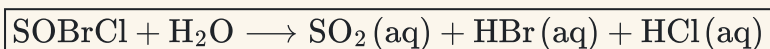
- **i)** Chloride $[\text{Cl}^-]$, bromide $[\text{Br}^-]$, and iodide $[\text{I}^-]$.
- **ii)** Sulphate $[\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$.
- **iii)** Fluoride $[\text{F}^-]$.
- **iv)** Sulphite $[\text{O}^-]\text{S}(=\text{O})[\text{O}^-]$ is oxidized to sulphate, which then precipitates:



- **v)** Iodide gives copper(I) iodide and iodine:



- **3.4** The possible compounds are **thionyl bromide**, SOBr_2 , $\text{O}=\text{S}(\text{Br})\text{Br}$, and **thionyl bromide chloride**, SOBrCl , $\text{O}=\text{S}(\text{Cl})\text{Br}$.
- **3.5** The intended compound is **thionyl bromide chloride**, $\boxed{\text{SOBrCl}}$. The printed masses have a small numerical inconsistency, discussed below.
- **3.6**



Solution

3.1 — Lewis structures

The total valence-electron counts are:

Molecule	Valence electrons
SCl_2	$6 + 2(7) = 20$
SO_3	$6 + 3(6) = 24$
SO_2ClF	$6 + 2(6) + 2(7) = 32$
SF_4	$6 + 4(7) = 34$
SBrF_5	$6 + 6(7) = 48$

Using the bonds and lone pairs listed in the Answers accounts for every electron. For example, in SF_4 , the four bonds use eight electrons, the fluorine lone pairs use twenty-four, and the remaining two form one sulphur lone pair.

These are conventional expanded-octet Lewis structures for sulphur where necessary. SMILES records connectivity and formal bond orders; it does not explicitly show the lone pairs or the geometries described below. Ionic SMILES used later likewise do not describe a solid's crystal lattice.

3.2 — Molecular geometries

In VSEPR counting, each single or multiple bond constitutes one electron domain.

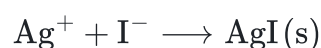
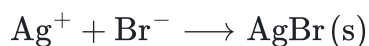
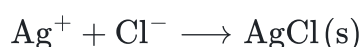
Molecule	VSEPR type	Precise description of the requested drawing
SCl ₂	AX ₂ E ₂	Four electron domains have a tetrahedral arrangement. Two positions contain chlorine atoms and two contain lone pairs, giving a bent molecule. The ideal tetrahedral reference angle is 109.5°.
SO ₃	AX ₃	Put sulphur at the centre of an equilateral triangle, with the three oxygen atoms at its vertices. All four atoms are coplanar; the angles are 120°.
SO ₂ ClF	AX ₄	Put sulphur at the centre of a tetrahedron and the two oxygen atoms, chlorine, and fluorine at its four vertices. Ideal angles are 109.5°.
SF ₄	AX ₄ E	Start from a trigonal bipyramid. Put the lone pair in one equatorial position, two fluorines in the other equatorial positions, and two fluorines in the axial positions. This gives a seesaw: axial–axial 180°, equatorial–equatorial 120°, and axial–equatorial 90°.
SBrF ₅	AX ₆	Put sulphur at the centre of an octahedron. Place bromine above sulphur, one fluorine directly below, and the other four fluorines at the corners of a square in the perpendicular plane. Adjacent bonds make 90°, and opposite bonds make 180°.

The lone pair in SF₄ occupies an equatorial position because that position has only two 90° interactions with neighbouring domains, whereas an axial position would have three.

3.3 — Analytical tests

i) Nitric acid and silver nitrate

Silver(I) ions [Ag⁺] detect chloride, bromide, and iodide by precipitation:



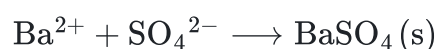
The products are:

- Silver chloride [Ag⁺] . [Cl[−]]: white.
- Silver bromide [Ag⁺] . [Br[−]]: cream or pale yellow.
- Silver iodide [Ag⁺] . [I[−]]: yellow.

Silver fluoride [Ag⁺] . [F[−]] is soluble, so this is not a fluoride test. Nitric acid O[N⁺] (=O) [O[−]] suppresses interference from sulphite precipitation without introducing a halide.

ii) Barium nitrate

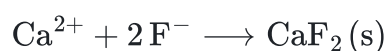
Barium ions [Ba²⁺] detect sulphate through formation of white, acid-insoluble barium sulphate [Ba²⁺] . [O[−]]S(=O)(=O)[O[−]]:



The acidity of the hydrolysed sample matters: sulphite does not give the same persistent, acid-insoluble precipitate.

iii) Neutralization and calcium nitrate

Calcium ions [Ca²⁺] detect fluoride by precipitation of calcium fluoride [Ca²⁺] . [F[−]] . [F[−]]:



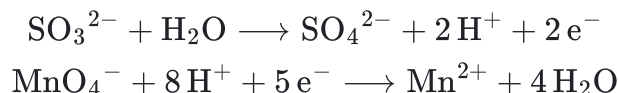
Neutralization prevents fluoride from remaining predominantly as hydrogen fluoride, HF . Ammonia NH_3 accepts a proton, forming ammonium $[\text{NH}_4^+]$:



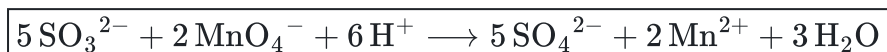
iv) Acidic permanganate, followed by barium nitrate

Permanganate $[\text{O}^-][\text{Mn}](=\text{O})(=\text{O})=\text{O}$ oxidizes sulphur(IV) to sulphur(VI) and is reduced to manganese(II), $[\text{Mn}^{2+}]$.

Using sulphite notation, the half-reactions are:



Multiplying the first by five and the second by two gives:

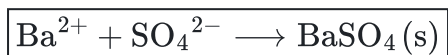


Here water is H_2O , and hydrogen ions are represented by $[\text{H}^+]$.

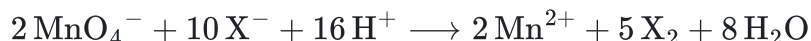
In acidic solution, sulphur(IV) occurs mainly as dissolved sulphur dioxide $\text{O}=\text{S}=\text{O}$ and hydrogen sulphite $\text{O}=\text{S}(\text{O})[\text{O}^-]$, rather than free sulphite. An equivalent equation using hydrogen sulphite is:



The subsequent precipitation is:



Permanganate can also oxidize bromide and iodide:

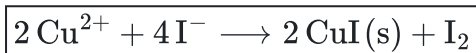


For $\text{X} = \text{Br}$ or I , the products are bromine Br_2 or iodine I_2 . Under sufficiently strongly acidic conditions, chloride can also be oxidized by this equation to chlorine Cl_2 .

Thus, disappearance of the permanganate colour alone is not specific to sulphur(IV). Formation of sulphate, demonstrated by the subsequent barium precipitate, supplies the decisive additional evidence.

v) Copper(II) nitrate

Copper(II) ions $[\text{Cu}^{2+}]$ oxidize iodide to iodine. The reduced copper precipitates as white copper(I) iodide $[\text{Cu}^+][\text{I}^-]$:



This is the diagnostic iodide reaction relevant here.

3.4 — Possible compounds

Under the qualitative-test assumptions of the problem:

1. The yellowish silver precipitate indicates bromide and/or iodide. Chloride may also be present in a mixed precipitate.
2. The negative copper(II) test excludes iodide. Therefore, bromide is present.
3. The negative calcium test excludes fluoride.

4. No initial barium precipitate means sulphate is absent. Formation of barium sulphate after oxidation shows that the original hydrolysate contains sulphur(IV).

Because hydrolysis involved no oxidation or reduction, the sulphur in the original compound also had oxidation state +4.

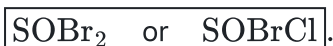
Let its composition be SO_aX_b , where X represents monovalent halogens. With oxygen at -2 and halogens at -1 ,

$$2a + b = 4.$$

Both oxygen and halogen must be present, so $a \geq 1$ and $b \geq 1$. The only integer solution is

$$a = 1, \quad b = 2.$$

The compound is consequently a thionyl dihalide. Since bromine must occur, chlorine may occur, and fluorine and iodine are excluded, the possibilities are:



Their names and SMILES are thionyl bromide $\text{O}=\text{S}(\text{Br})\text{Br}$ and thionyl bromide chloride $\text{O}=\text{S}(\text{Cl})\text{Br}$. The analysis does not determine an absolute configuration at sulphur in the mixed halide.

3.5 — Quantitative identification

The mass of original substance represented by the aliquot is

$$m_{\text{aliquot}} = 7.190 \text{ g} \left(\frac{25.00 \text{ cm}^3}{250.0 \text{ cm}^3} \right) = 0.7190 \text{ g}.$$

The problem gives no atomic masses. Using standard rounded atomic masses in g mol^{-1} ,

$$\begin{aligned} M(\text{S}) &= 32.06, & M(\text{O}) &= 16.00, \\ M(\text{Cl}) &= 35.45, & M(\text{Br}) &= 79.90, & M(\text{Ag}) &= 107.87, \end{aligned}$$

gives

$$\begin{aligned} M(\text{AgCl}) &= 143.32 \text{ g mol}^{-1}, \\ M(\text{AgBr}) &= 187.77 \text{ g mol}^{-1}. \end{aligned}$$

For **thionyl bromide**, each mole gives two moles of silver bromide:

$$m_{\text{precipitate}} = \frac{0.7190 \text{ g}}{207.86 \text{ g mol}^{-1}} (2 \times 187.77 \text{ g mol}^{-1}) = 1.299 \text{ g}.$$

For **thionyl bromide chloride**, each mole gives one mole each of silver bromide and silver chloride:

$$m_{\text{precipitate}} = \frac{0.7190 \text{ g}}{163.41 \text{ g mol}^{-1}} (187.77 + 143.32) \text{ g mol}^{-1} = 1.457 \text{ g}.$$

Candidate	Predicted precipitate mass
SOBr_2	1.299 g
SOBrCl	1.457 g
Experimental value	1.452 g

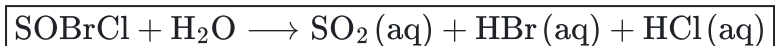
The reported value clearly selects the mixed halide as the intended answer:



Nevertheless, its predicted mass differs from the printed value by approximately 0.0048 g, or 0.33%. Ordinary atomic-mass rounding does not explain that difference.

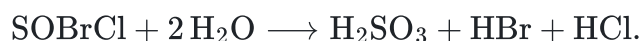
3.6 — Hydrolysis

Thionyl bromide chloride hydrolyses to sulphur dioxide, hydrogen bromide Br, and hydrogen chloride Cl:



The aqueous designation respects the statement that all products dissolved.

Using the conventional sulphurous-acid representation, sulphurous acid $\text{O}=\text{S}(\text{O})\text{O}$, the same hydrolysis is commonly written:



Here H_2SO_3 denotes the aqueous sulphur(IV) system. Sulphur remains at oxidation state +4, so the hydrolysis involves no redox change.

The solution was checked against the official solution.

Problem 4: Platinum chemistry and the catalytic oxidation of carbon monoxide

Platinum(IV) oxide is not found in the nature, but it can be prepared in a laboratory. Solid platinum(IV) oxide is in equilibrium with platinum metal and oxygen gas at 1 atm ($= 1.01325 \times 10^5$ Pa) and 650 °C.

4.1 This suggests that the conditions on the Earth, when the minerals we know were formed, were:

- [1] $p(\text{O}_2) = 1 \text{ atm}, t = 650 \text{ °C};$
- [2] $p(\text{O}_2) < 1 \text{ atm}, t < 650 \text{ °C};$
- [3] $p(\text{O}_2) > 1 \text{ atm}, t < 650 \text{ °C};$
- [4] $p(\text{O}_2) < 1 \text{ atm}, t > 650 \text{ °C};$
- [5] $p(\text{O}_2) > 1 \text{ atm}, t > 650 \text{ °C}$

Mark the most probable alternative [1] – [5] on the answer sheet. Please note that the marking of only one alternative will be accepted.

4.2 What are ΔG and K_p for the formation of platinum(IV) oxide at oxygen pressure of 1 atm and temperature of 650 °C?

The preparation of platinum(IV) oxide involves boiling of a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process $\text{PtO}_2 \cdot n \text{H}_2\text{O}$ is formed and this is in turn converted to platinum(IV) oxide upon subsequent filtering and heat treatment. In the following we assume $n = 4$.

$\text{PtO}_2 \cdot 4 \text{H}_2\text{O}$ or $\text{Pt}(\text{OH})_4 \cdot 2 \text{H}_2\text{O}$ can be dissolved in acids and strong bases.

4.3 Write the balanced equations for the preparation of platinum(IV) oxide according to the procedure given above.

4.4 Write the balanced equations for the dissolution of $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$ in both hydrochloric acid and sodium hydroxide.

Platinum is mainly found in the nature as the metal (in mixture or in alloying with other precious metals). Platinum is dissolved in aqua regia under the formation of hexachloroplatinate(IV) ions. Aqua regia is a mixture of concentrated hydrochloric and nitric acids in proportion 3 : 1, and of the nitrosylchloride (NOCl) and the atomic chlorine which are formed upon the mixing. The latter is believed to be the active dissolving component.

The hexachloroplatinate(IV) ions can be precipitated as diammonium hexachloroplatinate(IV) and by thermal decomposition of this compound, finely powdered platinum and gaseous products are formed.

4.5 Write the balanced equations for the formation of aqua regia and its reaction with platinum.

4.6 Write the balanced equation of the thermal decomposition of diammonium hexachloroplatinate(IV) at elevated temperature.

From diammonium hexachloroplatinate(IV) we can prepare $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ which occurs in cis ($\Delta_f H^0 = -467.4 \text{ kJ mol}^{-1}$, $\Delta_f G^0 = -228.7 \text{ kJ mol}^{-1}$) and trans ($\Delta_f H^0 = -480.3 \text{ kJ mol}^{-1}$, $\Delta_f G^0 = -222.8 \text{ kJ mol}^{-1}$) form.

4.7 The occurrence of the isomers shows that $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has geometry:

- [1] linear,
- [2] planar,
- [3] tetrahedral,
- [4] octahedral geometry.

Mark the correct alternative of [1] – [4] on the answer sheet.

4.8 Is the cis form or trans form thermodynamically more stable?

Platinum is used as a catalyst in modern automobiles. In the catalyst carbon monoxide ($\Delta_f H^0 = -110.5 \text{ kJ mol}^{-1}$, $\Delta_f G^0 = -137.3 \text{ kJ mol}^{-1}$) reacts with oxygen to carbon dioxide ($\Delta_f H^0 = -393.5 \text{ kJ mol}^{-1}$, $\Delta_f G^0 = -394.4 \text{ kJ mol}^{-1}$).

4.9 Is the reaction spontaneous at 25 °C?

- [1] yes, or
- [2] no.

Is the reaction:

- [3] endothermic, or
- [4] exothermic?

Calculate ΔS° for the reaction.

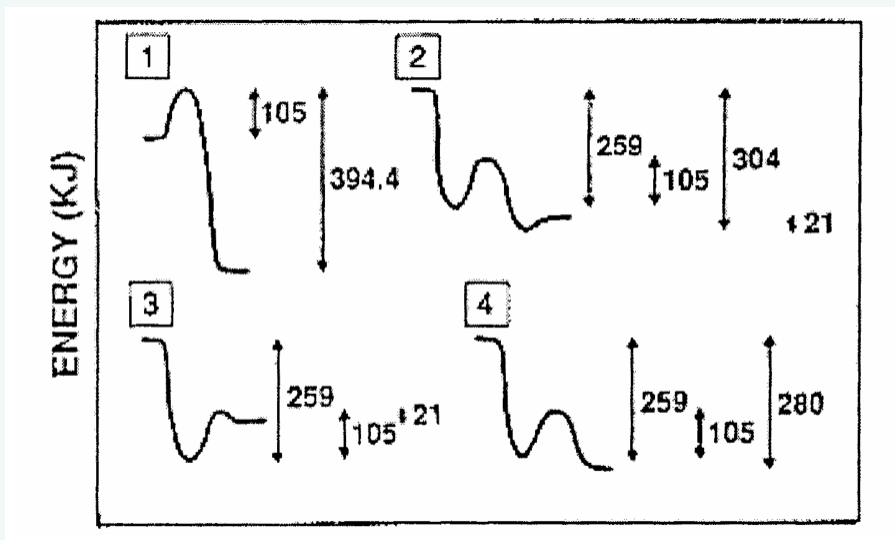
Establish whether the entropy of the reaction system

- [5] increases, or
- [6] decreases.

4.10 Establish an expression for the temperature dependence of the equilibrium constant in this case.

The overall catalytic reaction is simple, whereas the reaction mechanism in the homogeneous phase is very complicated with a large number of reaction steps, and the course is difficult to control owing to a distinct chain character. With platinum as catalyst the significant reaction steps are: (i) Adsorption of CO and adsorption/dissociation of O₂ ($\Delta H = -259$ kJ per mol CO + O), (ii) their activation (105 kJ per mol CO + O) and (iii) the reaction and the desorption of CO₂ ($\Delta H = 21$ kJ per mol CO₂).

A one-dimensional energy-diagram for the platinum catalyzed oxidation of carbon monoxide to dioxide can be represented as:



4.11 Mark the correct alternative of [1] – [4] on the answer sheet.

Official English text of the problem.

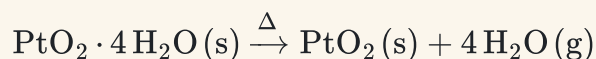
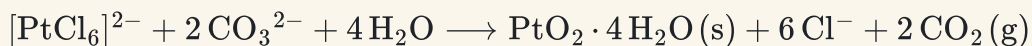
Answers

Species names and SMILES are collected in the Solution.

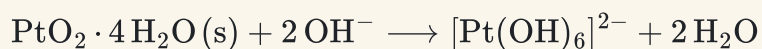
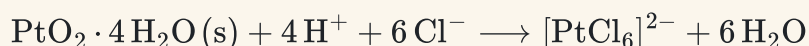
- 4.1: [4], $p(\text{O}_2) < 1 \text{ atm}$, $t > 650^\circ\text{C}$, using the intended qualitative oxide-stability argument.

- 4.2: $\Delta_r G = 0$, $K_p = 1$, taking $p^\circ = 1 \text{ atm}$.

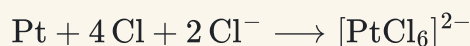
- 4.3:



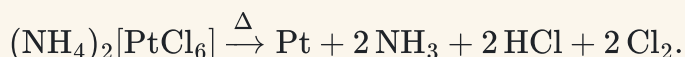
- 4.4:



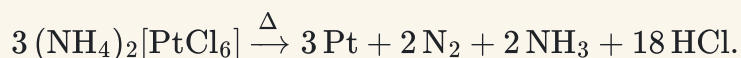
- 4.5: In the atomic-chlorine description specified in the problem,



- **4.6:** A formal primary decomposition is



Allowing subsequent reaction between ammonia and chlorine gives the nitrogen-forming net balance



The unspecified gas products require the qualification discussed below.

- **4.7: [2]**, specifically **square planar**.
- **4.8: Cis**, because its standard Gibbs energy of formation is lower.
- **4.9: [1] yes; [4] exothermic; [6] entropy decreases.** For $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$,

$$\Delta_r H^\circ = -283.0 \text{ kJ mol}^{-1}, \quad \Delta_r G^\circ = -257.1 \text{ kJ mol}^{-1}, \quad \Delta_r S^\circ = -86.9 \text{ J mol}^{-1} \text{ K}^{-1}.$$

For $2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$, these values double.

- **4.10:** For the reaction producing one mole of carbon dioxide, assuming temperature-independent reaction enthalpy and entropy,

$$K_p(T) \simeq \exp\left(\frac{3.404 \times 10^4 \text{ K}}{T} - 10.45\right).$$

Thus K_p decreases as temperature increases.

- **4.11: [2]**. Relative energy levels are 0, −259, −154, −304, −283 kJ mol^{−1}, in reaction order.

Solution

Chemical names and SMILES

The following identifiers cover the species used in the answers. Dative bonds are written with →. The platinum(IV) complexes are octahedral; the square-planar stereochemistry of the two platinum(II) isomers is specified explicitly.

Platinum metal and the oxides are extended solids, so their entries represent an atom or formal formula-unit composition, not a discrete molecular structure. SMILES also do not specify gas spin states or the adsorption sites on the catalyst.

Species and name	SMILES
Pt, platinum	[Pt]
PtO ₂ , platinum(IV) oxide, formal composition	[Pt+4].[O-2].[O-2]
PtO ₂ · 4 H ₂ O, hydrated platinum(IV) oxide, formal composition	[Pt+4].[O-2].[O-2].O.O.O.O
[PtCl ₆] ^{2−} , hexachloroplatinate(IV) ion	[Cl-]>[Pt+4](<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])
[Pt(OH) ₆] ^{2−} , hexahydroxoplatinate(IV) ion	[OH-]>[Pt+4](<-[OH-])(<-[OH-])(<-[OH-])(<-[OH-])(<-[OH-])
(NH ₄) ₂ [PtCl ₆], diammonium hexachloroplatinate(IV)	[NH4+].[NH4+].[Cl-]>[Pt+4](<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])(<-[Cl-])

Species and name	SMILES
cis-Pt(NH ₃) ₂ Cl ₂ , cis-diamminedichloridoplatinum(II), cisplatin	[NH3]->[Pt@SP1+2](<-[NH3])(<-[Cl-])<-[Cl-]
trans-Pt(NH ₃) ₂ Cl ₂ , trans-diamminedichloridoplatinum(II), transplatin	[NH3]->[Pt@SP2+2](<-[NH3])(<-[Cl-])<-[Cl-]
Na ₂ CO ₃ , sodium carbonate	[Na+].[Na+].[O-]C(=O)[O-]
NaOH, sodium hydroxide	[Na+].[OH-]
CO ₃ ²⁻ , carbonate ion	[O-]C(=O)[O-]
H ⁺ , hydrogen ion	[H+]
Cl ⁻ , chloride ion	[Cl-]
OH ⁻ , hydroxide ion	[OH-]
NH ₄ ⁺ , ammonium ion	[NH4+]
NH ₄ Cl, ammonium chloride	[NH4+].[Cl-]
H ₂ O, water	O
HCl, hydrogen chloride; hydrochloric acid when dissolved in water	Cl
HNO ₃ , nitric acid	O[N+](=O)[O-]
NOCl, nitrosyl chloride	O=NC1
Cl, atomic chlorine	[Cl]
Cl ₂ , molecular chlorine	ClCl
NH ₃ , ammonia	N
N ₂ , nitrogen	N#N
O ₂ , oxygen	O=O
O, atomic oxygen	[O]
CO, carbon monoxide	[C-]#[O+]
CO ₂ , carbon dioxide	O=C=O

4.1

Consider the equilibrium



Lowering the oxygen partial pressure favors decomposition, which produces oxygen. Using the intended assumption that oxide formation is exothermic, increasing the temperature also favors decomposition.

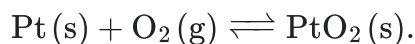
Thus the combination that most clearly favors native platinum over its oxide is

$$p(\text{O}_2) < 1 \text{ atm}, \quad t > 650^\circ\text{C},$$

namely **[4]**.

4.2

For formation,



The reaction Gibbs energy is zero at equilibrium:

$$\boxed{\Delta_r G = 0}.$$

Pure solid activities equal unity. Defining a dimensionless equilibrium constant with $p^\circ = 1 \text{ atm}$,

$$K_p = \frac{a(\text{PtO}_2)}{a(\text{Pt})[p(\text{O}_2)/p^\circ]} = \frac{p^\circ}{p(\text{O}_2)}.$$

Since the equilibrium oxygen pressure is 1 atm,

$$\boxed{K_p = 1}.$$

With this standard-pressure convention, $\Delta_r G^\circ = -RT \ln K_p = 0$ as well.

If an unnormalized, dimensional pressure quotient is used instead, its value is 1 atm^{-1} .

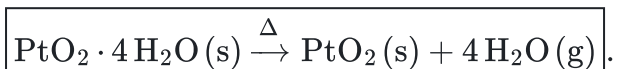
4.3

Carbonate acts as a base, allowing precipitation of the hydrous oxide while carbon dioxide is released. The net ionic equation is



Both sides have charge -6 , and all atoms balance. Sodium ions are spectators. Platinum remains in oxidation state $+IV$, so this is not a redox reaction.

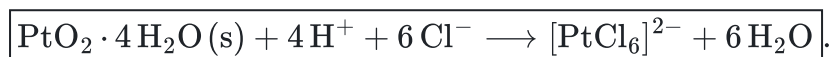
After filtration, heating removes the water:



4.4

The hydrated oxide is amphoteric.

In hydrochloric acid, protons convert the oxide/hydroxide groups into water, and chloride coordinates the platinum:



The total charge is -2 on either side.

In sodium hydroxide, the soluble product is the hexahydroxoplatinate(IV) ion:



Again, both sides have charge -2 . Platinum remains $+IV$ in both reactions.

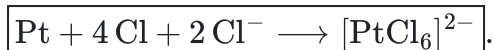
4.5

Following the problem's explicit description in terms of atomic chlorine, mixing the acids gives



Nitrogen is reduced from $+V$ in nitric acid to $+III$ in nitrosyl chloride. Two chloride ions are correspondingly oxidized to two neutral chlorine atoms.

Platinum then reacts according to

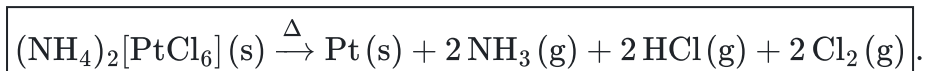


Platinum loses four electrons, becoming platinum(IV); four chlorine atoms each gain one electron. Two further chloride ions complete the six-coordinate, octahedral complex.

These equations use the atomic-chlorine model stated in the question; they do not establish a detailed dissolution mechanism.

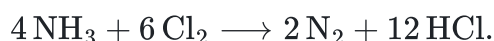
4.6

A balanced formal decomposition into platinum, ammonia, hydrogen chloride and chlorine is

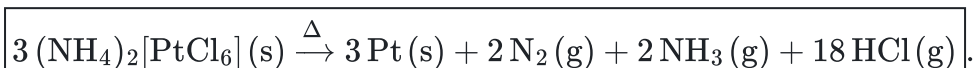


Here platinum is reduced from $+IV$ to zero, and four chloride ligands are oxidized to two chlorine molecules. The remaining atoms give ammonia and hydrogen chloride.

However, ammonia and chlorine can react further. A nitrogen-forming balance is

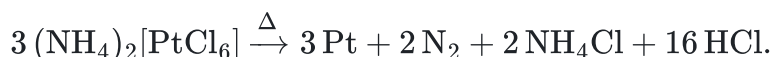


Adding this to three times the formal decomposition above gives



For this net reaction, four nitrogen atoms are oxidized from $-III$ to zero, supplying the twelve electrons required to reduce three platinum(IV) centers.

Grouping two ammonia and two hydrogen chloride molecules as ammonium chloride gives the corresponding formula-unit balance



At elevated temperature, the volatile ammonium chloride can be represented through its dissociation into ammonia and hydrogen chloride. These equations distinguish primary decomposition from secondary gas chemistry; the statement does not specify the final gas composition.

4.7

There are four ligands around platinum. In a tetrahedral arrangement, all pairs of ligand positions are equivalent, so a complex containing two ligands of each kind cannot have distinct cis and trans forms.

A square-planar arrangement permits:

- **Cisplatin:** the two chloride ligands are adjacent, with a $\text{Cl}-\text{Pt}-\text{Cl}$ angle of approximately 90° ; the ammonia ligands are also adjacent.
- **Transplatin:** the chloride ligands are opposite, with a $\text{Cl}-\text{Pt}-\text{Cl}$ angle of 180° ; the ammonia ligands are also opposite.

All four donor atoms and the platinum atom lie in one plane. Therefore the answer is **[2], planar**, specifically **square planar**. The stereochemical SMILES are given in the identifier table.

4.8

Thermodynamic stability at fixed temperature and pressure is determined by Gibbs energy. For cis-to-trans conversion,

$$\begin{aligned}
 \Delta_r G^\circ &= \Delta_f G^\circ(\text{trans}) - \Delta_f G^\circ(\text{cis}) \\
 &= -222.8 - (-228.7) \\
 &= +5.9 \text{ kJ mol}^{-1}.
 \end{aligned}$$

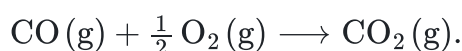
Thus the conversion to trans is unfavorable under the standard conditions of the supplied data:

The cis form is thermodynamically more stable.

Although the trans form has the lower enthalpy of formation, its entropy contribution makes its Gibbs energy higher.

4.9

Use the reaction normalized to one mole of carbon monoxide:



The standard formation enthalpy and Gibbs energy of elemental oxygen in its standard state are zero.

Hence

$$\begin{aligned}
 \Delta_r H^\circ &= -393.5 - (-110.5) \\
 &= \boxed{-283.0 \text{ kJ mol}^{-1}}, \\
 \Delta_r G^\circ &= -394.4 - (-137.3) \\
 &= \boxed{-257.1 \text{ kJ mol}^{-1}}.
 \end{aligned}$$

Since $\Delta_r G^\circ < 0$, the forward reaction is spontaneous under standard conditions at 25 °C: **[1]**. Since $\Delta_r H^\circ < 0$, it is exothermic: **[4]**.

Using

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

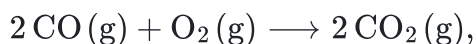
at $T = 298.15 \text{ K}$,

$$\begin{aligned}
 \Delta_r S^\circ &= \frac{-283.0 - (-257.1)}{298.15} \text{ kJ mol}^{-1} \text{ K}^{-1} \\
 &= \boxed{-86.9 \text{ J mol}^{-1} \text{ K}^{-1}}.
 \end{aligned}$$

The system's entropy decreases: **[6]**, consistent with the reduction from 1.5 moles of gas to 1 mole of gas.

This does not conflict with spontaneity: the released heat increases the surroundings' entropy by more than the system's entropy decreases.

For the integer-coefficient equation



the corresponding values are

$$\Delta_r H^\circ = -566.0 \text{ kJ mol}^{-1}, \quad \Delta_r G^\circ = -514.2 \text{ kJ mol}^{-1}, \quad \Delta_r S^\circ = -173.7 \text{ J mol}^{-1} \text{ K}^{-1},$$

where "per mole" now refers to one mole of reaction as written.

4.10

For the one-carbon-monoxide reaction,

$$K_p = \frac{p(\text{CO}_2)/p^\circ}{[p(\text{CO})/p^\circ][p(\text{O}_2)/p^\circ]^{1/2}}.$$

The exact van 't Hoff relation is

$$\boxed{\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ(T)}{RT^2}}.$$

If $\Delta_r H^\circ$ is treated as constant, integration gives

$$\boxed{\ln \frac{K_p(T)}{K_p(T_0)} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}.$$

Equivalently, taking both reaction enthalpy and entropy as temperature independent,

$$\ln K_p = -\frac{\Delta_r G^\circ}{RT} = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}.$$

Using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$\ln K_p(T) = \frac{283000}{8.314 T} - \frac{86.869}{8.314},$$

so

$$\boxed{K_p(T) \simeq \exp \left(\frac{3.404 \times 10^4 \text{ K}}{T} - 10.45 \right)}.$$

At 298.15 K, this gives approximately

$$K_p = 1.1 \times 10^{45}.$$

Because the reaction is exothermic, $d \ln K_p / dT < 0$: raising the temperature decreases the equilibrium constant.

If the reaction is instead written as $2 \text{ CO} + \text{O}_2 \longrightarrow 2 \text{ CO}_2$, its equilibrium constant is the square of the one above:

$$K_{p,2}(T) \simeq \exp \left(\frac{6.808 \times 10^4 \text{ K}}{T} - 20.90 \right).$$

4.11

Take the gaseous reactants and free platinum surface as the zero of energy, per mole of carbon monoxide oxidized.

1. Adsorption and oxygen dissociation lower the energy by 259 kJ mol^{-1} :

$$E_{\text{adsorbed reactants}} = -259 \text{ kJ mol}^{-1}.$$

2. The activation barrier is 105 kJ mol^{-1} above those adsorbed reactants:

$$E_{\text{transition state}} = -259 + 105 = -154 \text{ kJ mol}^{-1}.$$

3. The final gaseous product must lie at the overall reaction enthalpy calculated in 4.9:

$$E_{\text{gaseous product}} = -283 \text{ kJ mol}^{-1}.$$

4. Desorption requires 21 kJ mol^{-1} , so the adsorbed carbon dioxide lies below the gaseous product:

$$E_{\text{adsorbed product}} = -283 - 21 = -304 \text{ kJ mol}^{-1}.$$

The required profile therefore starts at zero, falls to -259 , rises to -154 , falls to -304 , and finally rises to -283 kJ mol^{-1} .

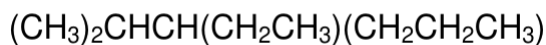
This is **diagram [2]**. The catalyst provides a reaction pathway with surface intermediates but does not change the overall reaction enthalpy or equilibrium constant.

The solution was checked against the official solution.

Problem 5: Organic chemistry multiple-choice questions

There is only one correct answer to each question

5.1 What is the correct systematic name (IUPAC name) for the compound below?

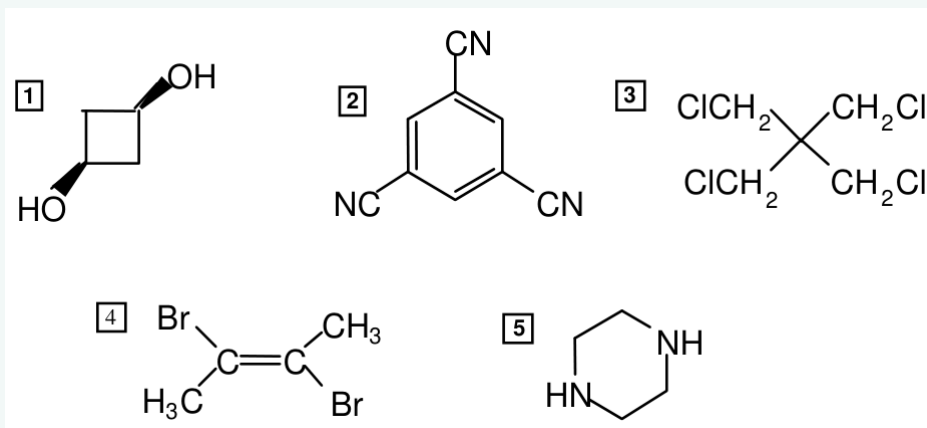


1. 3-Isopropylhexane
2. 2-Methyl-3-propylpentane
3. Ethyl isopropyl propyl methane
4. 3-Hexylpropane
5. 3-Ethyl-2-methylhexane

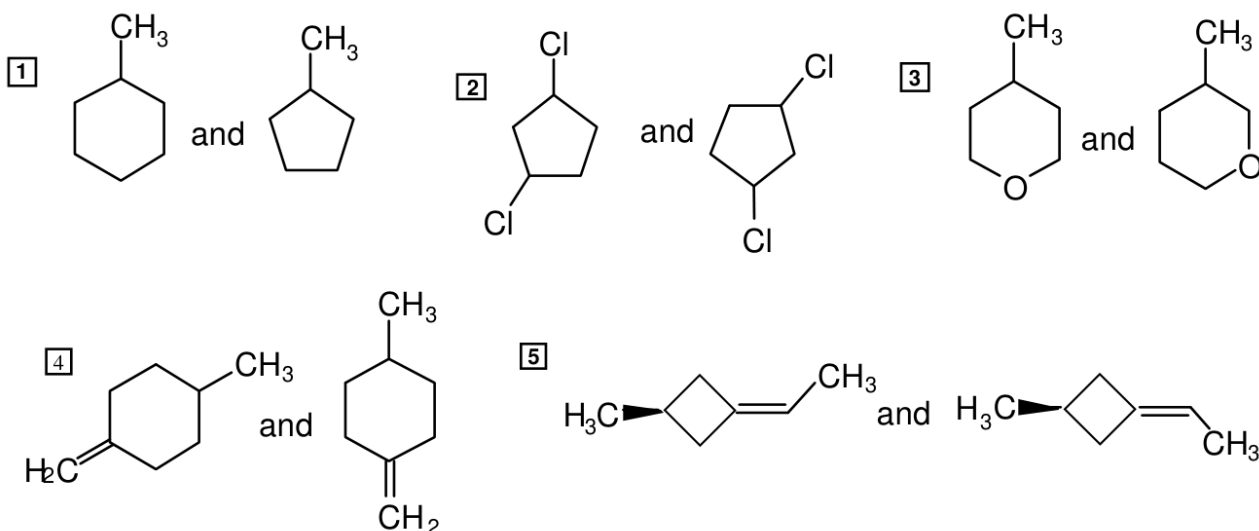
5.2 How many isomers, including stereoisomers, containing only saturated carbon atoms, are there for C_5H_{10} ?

1. 4 isomers
2. 5 isomers
3. 6 isomers
4. 7 isomers
5. 8 isomers

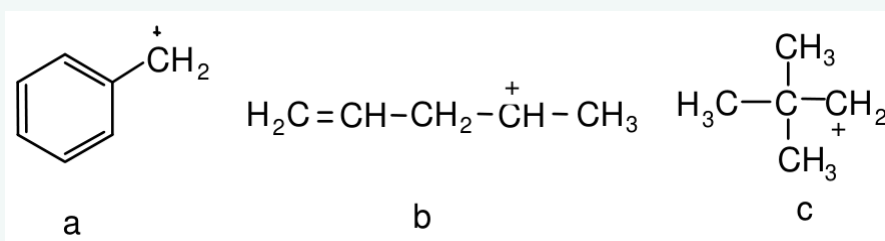
5.3 Which one of the following compounds has a dipole moment significantly different from zero?



5.4 Which of the following is a pair of structural isomers?

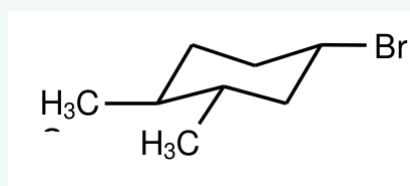


5.5 Which of the following five options is the correct order of relative stabilities of cations a, b and c as written below (most stable first)?



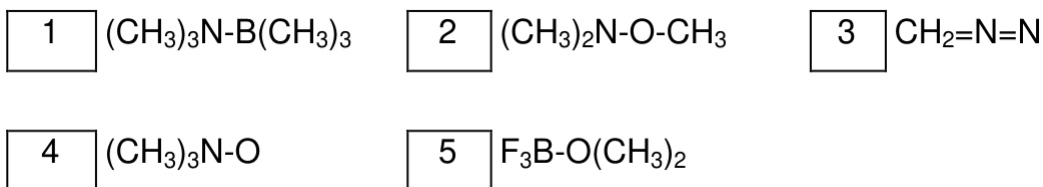
1. $a > b > c$
2. $b > c > a$
3. $c > a > b$
4. $a > c > b$
5. $b > a > c$

5.6 What is the correct stereochemical descriptor of the optically active compound drawn below?



1. 1*R*, 3*R*, 4*R*
2. 1*R*, 3*R*, 4*S*
3. 1*R*3*S*, 4*R*
4. 1*S*, 3*S*, 4*R*
5. 1*S*, 3*S*, 4*S*

5.7 All the molecules drawn below are neutral compounds. Which one does **not** contain a formal positive charge and a formal negative charge?



Official English text of the problem.

Answers

- **5.1 — Option 5:** 3-ethyl-2-methylhexane, CC(C)C(CC)CCC.
- **5.2 — Option 4:** 7 isomers.
- **5.3 — Option 1:** cis-cyclobutane-1,3-diol, O[C@H]1C[C@@H](O)C1.
- **5.4 — Option 3:** 4-methyloxane, CC1CCOCC1, and 3-methyloxane, CC1COCCC1.
- **5.5 — Option 1:** $a > b > c$.
- **5.6 — Option 5:** (1*S*, 3*S*, 4*S*), using the numbering implicit in the choices.
- **5.7 — Option 2:** N,N,O-trimethylhydroxylamine, CN(C)OC.

Solution

5.1 — Selecting and numbering the parent chain

The longest continuous carbon chain contains six carbon atoms. Among the possible six-carbon chains, select the one giving the greatest number of substituents:



This chain has a methyl group and an ethyl group. Numbering from the nearer end gives locants 2, 3, rather than 4, 5.

The substituent names are written alphabetically, so ethyl precedes methyl. The name is therefore **3-ethyl-2-methylhexane**, option 5.

The alternative six-carbon chain underlying "3-isopropylhexane" has only one substituent and is not the correct parent-chain selection.

5.2 — Counting saturated isomers

The degree of unsaturation is

$$\text{DBE} = \frac{2(5) + 2 - 10}{2} = 1.$$

Since all carbon atoms must be saturated, this degree of unsaturation must be a ring, rather than a double bond. Thus, the compounds are monocyclic cycloalkanes.

The possibilities are:

Isomer	SMILES
Cyclopentane	<chem>C1CCCC1</chem>
Methylcyclobutane	<chem>CC1CCC1</chem>

Isomer	SMILES
Ethylcyclopropane	<chem>CCC1CC1</chem>
1,1-Dimethylcyclopropane	<chem>CC1(C)CC1</chem>
cis-(1R,2S)-1,2-Dimethylcyclopropane	<chem>C[C@H]1[C@@H](C)C1</chem>
trans-(1R,2R)-1,2-Dimethylcyclopropane	<chem>C[C@H]1[C@H](C)C1</chem>
trans-(1S,2S)-1,2-Dimethylcyclopropane	<chem>C[C@@H]1[C@@H](C)C1</chem>

The cis-1,2-dimethyl compound is meso: its mirror image is superimposable. The trans compound exists as two distinct enantiomers.

Consequently,

$$N = 4 + 1 + 2 = \boxed{7}.$$

Conformations that interconvert by ordinary ring motion are not counted separately. The answer is option **4**.

5.3 — Molecular dipoles

In option **1**, both hydroxyl groups are shown with solid wedges, so they lie on the same face of the ring. The molecule is **cis-cyclobutane-1,3-diol**.

The components of the two hydroxyl-group dipoles perpendicular to the ring reinforce one another. They therefore produce a substantial resultant dipole.

The other choices illustrate cancellation in symmetric molecular arrangements:

Option	Compound and SMILES	Symmetry argument
2	Benzene-1,3,5-tricarbonitrile, <chem>N#Cc1cc(C#N)cc(C#N)c1</chem>	The three equivalent nitrile-group dipoles are arranged at 120° and cancel.
3	Tetrakis(chloromethyl)methane, <chem>ClCC(Cl)(Cl)CCl</chem>	A symmetric arrangement of the four equivalent arms permits their dipoles to cancel.
4	(E)-2,3-Dibromobut-2-ene, <chem>C/C(Br)=C(Br)/C</chem>	The trans arrangement gives opposing bond dipoles and a centrosymmetric molecular framework.
5	Piperazine, <chem>N1CCNCC1</chem>	Its symmetric chair conformation has opposing amine groups and a center of inversion.

Thus, the intended answer is **option 1**. The conformations used for compounds 3 and 5 are not specified by their SMILES.

5.4 — Constitutional isomerism

Structural, or constitutional, isomers have the same molecular formula but different atom-to-atom connections.

In option **3**, both compounds have molecular formula $C_6H_{12}O$. Numbering the six-membered heterocycle from oxygen as position 1:

- The left structure has its methyl group at position 4: **4-methyloxane**, CC1CCOCC1.
- The right structure has its methyl group at position 3: **3-methyloxane**, CC1COCCC1.

Moving the methyl attachment from position 4 to position 3 changes connectivity. These are therefore constitutional isomers.

Option 1 has different molecular formulas for its two members. Options 2, 4 and 5 retain the same connectivity within each pair. The answer is **option 3**.

5.5 — Carbocation stability

The three cations are:

Cation	Identification and SMILES	Principal stabilization
<i>a</i>	Benzyl cation, <chem>[CH2+]c1ccccc1</chem>	Resonance delocalization into the aromatic ring
<i>b</i>	Pent-4-en-2-yl cation, <chem>C=CC[CH+]C</chem>	A secondary carbocation, stabilized by adjacent alkyl groups
<i>c</i>	Neopentyl cation, <chem>CC(C)(C)[CH2+]</chem>	A primary carbocation without adjacent carbon–hydrogen bonds for ordinary C–H hyperconjugation

The benzyl cation is most stable because its vacant *p* orbital is conjugated with the aromatic ring, distributing the positive charge over several atoms.

Cation *b* is **homoallylic**, not allylic: a saturated methylene group separates the double bond from the positively charged carbon. It therefore lacks ordinary allylic resonance stabilization, but its secondary substitution still makes it more stable than *c*.

The phrase “as written” excludes stabilization obtained by rearranging a cation into a different structure. Hence,

$$a > b > c,$$

which is option 1.

5.6 — Absolute configuration

Use the numbering implicit in the choices: the bromine-bearing carbon is C1; proceeding along the lower edge of the chair gives C2, methyl-bearing C3, and methyl-bearing C4.

All three drawn substituents are **equatorial**. Bromine at C1 and methyl at C3 are on the same face; methyl at C4 is on the opposite face.

The Cahn–Ingold–Prelog priorities are:

Center	Priorities, highest to lowest	Configuration
C1	Br > ring path through C2 > ring path through C6 > H	<i>S</i>
C3	Ring path through C4 > ring path through C2 > methyl > H	<i>S</i>
C4	Ring path through C3 > ring path through C5 > methyl > H	<i>S</i>

At C1, the two ring paths initially tie. The path through C2 reaches methyl-substituted C3 first and therefore takes priority over the path through C6.

At C3, the adjacent C4 is attached to two other carbon atoms and one hydrogen, whereas C2 is attached to one other carbon and two hydrogens. Thus, the C4 path has higher priority. The analogous comparison at C4 favors the C3 path.

To make the spatial assignment explicit, an equivalent planar hexagon, numbered clockwise with C1 at the right, has:

- a dashed bromine bond at C1;
- a dashed methyl bond at C3;
- a solid-wedge methyl bond at C4.

At C1 and C3, the projected priority sequence is clockwise but hydrogen points toward the viewer, so the assignment is reversed to *S*. At C4, hydrogen points away and the sequence is counterclockwise, also giving *S*.

Therefore,

$$(1S, 3S, 4S),$$

option 5.

With the lowest-locant numbering used for its systematic name, the molecule is **(1*S*,2*S*,4*S*)-4-bromo-1,2-dimethylcyclohexane**, Br[C@@H]1C[C@H](C)[C@@H](C)CC1. This SMILES specifies configuration; the drawing additionally specifies the chair conformation with all three substituents equatorial.

5.7 — Formal charges

For an atom,

$$FC = V - N_{\text{nonbonding}} - \frac{N_{\text{bonding}}}{2},$$

where *V* is the number of valence electrons of the neutral atom.

In **N,N,O-trimethylhydroxylamine**, CN(C)OC, nitrogen has three single bonds and one lone pair, while oxygen has two single bonds and two lone pairs:

$$FC(N) = 5 - 2 - 3 = 0, \quad FC(O) = 6 - 4 - 2 = 0.$$

Neither atom carries a formal charge.

For comparison, assigning formal charges to all five structures gives:

Option	Compound and charge-explicit SMILES	Formal charges
1	Trimethylamine–trimethylborane adduct, <chem>C[N+](C)(C)[B-](C)(C)C</chem>	Nitrogen +1, boron −1
2	N,N,O-Trimethylhydroxylamine, <chem>CN(C)OC</chem>	All atoms uncharged
3	Diazomethane, <chem>C=[N+]=[N-]</chem>	Central nitrogen +1, terminal nitrogen −1
4	Trimethylamine N-oxide, <chem>C[N+](C)(C)[O-]</chem>	Nitrogen +1, oxygen −1
5	Boron trifluoride–dimethyl ether adduct, <chem>F[B-](F)(F)[O+](C)C</chem>	Boron −1, oxygen +1

In adducts 1 and 5, the nitrogen or oxygen lone pair is donated to boron. With that donor–acceptor bond represented as the drawn single bond, four-coordinate boron has formal charge −1; the donor atom has formal charge +1.

Thus, the only structure without separated formal charges is **option 2**.

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

Problem 6: Structure of an optically active compound C₁₂H₁₆O

An optical active compound **A** (C₁₂H₁₆O) shows amongst other a strong IR-absorption at 3000 – 3500 cm⁻¹, and two medium signals at 1580 and 1500 cm⁻¹. The compound does not react with 2,4-dinitrophenylhydrazine (2,4-D). Upon treatment with I₂/NaOH, **A** is oxidized and gives a positive iodoform reaction.

Ozonolysis of **A** (1. O₃; 2. Zn, H⁺) gives **B** (C₉H₁₀O) and **C** (C₃H₆O₂). Both **B** and **C** give precipitation when treated with 2,4-D, and only **C** gives positive reaction with Tollens reagent. Nitration of **B** (HNO₃/H₂SO₄) may give two mono-nitro compounds **D** and **E**, but in practical work only **D** is formed.

Acidification followed by heating of the product formed by the Tollens reaction on **C** gives compound **F** (C₆H₈O₄). The compound gives no absorption in IR above 3100 cm⁻¹.

6.1 Based on the above information draw the structure formula(e) for the compounds **A – F** and give the overall reaction scheme, including the (2,4-D) and the products of the Tollens and iodoform reactions.

6.2 Draw **C** in an R-configuration. Transform this into a Fischer projection formula and state whether it is a D or L configuration.

Official English text of the problem.

Answers

- 6.1.** The constitutional structures are:

Compound	Name and structure description	SMILES
A	4-(4-Methylphenyl)pent-3-en-2-ol; CH ₃ CH(OH)CH=C(CH ₃)C ₆ H ₄ CH ₃ , with the ring substituents para	<chem>CC(O)C=C(C)c1ccc(C)cc1</chem>
B	4-Methylacetophenone, or 1-(4-methylphenyl)ethan-1-one	<chem>CC(=O)c1ccc(C)cc1</chem>
C	2-Hydroxypropanal, commonly lactaldehyde	<chem>CC(O)C=O</chem>
D	1-(4-Methyl-3-nitrophenyl)ethan-1-one; the observed nitration product	<chem>CC(=O)c1cc([N+](=O)[O-])c(C)cc1</chem>
E	1-(4-Methyl-2-nitrophenyl)ethan-1-one; the alternative nitration product	<chem>CC(=O)c1c([N+](=O)[O-])cc(C)cc1</chem>
F	Lactide, or 3,6-dimethyl-1,4-dioxane-2,5-dione; a cyclic diester	<chem>CC1OC(=O)C(C)OC1=O</chem>

The absolute configuration and alkene geometry of **A** are unspecified. The table therefore leaves stereochemistry unassigned; explicit stereochemical possibilities are discussed below.

The requested reaction products are:

Reaction	Product name	SMILES
B with 2,4-D	4-Methylacetophenone 2,4-dinitrophenylhydrazone	<chem>CC(=NNc1ccc([N+](=O)[O-])cc1[N+](=O)[O-])c1ccc(C)cc1</chem>
C with 2,4-D	Lactaldehyde 2,4-dinitrophenylhydrazone	<chem>CC(O)C=NNc1ccc([N+](=O)[O-])cc1[N+](=O)[O-]</chem>
Tollens oxidation of C	Lactate, or 2-hydroxypropanoate	<chem>CC(O)C(=O)[O-]</chem>
Acidification of lactate	Lactic acid, or 2-hydroxypropanoic acid	<chem>CC(O)C(=O)O</chem>
Iodoform reaction of A	Sodium 3-(4-methylphenyl)but-2-enoate	<chem>[Na+].[O-]C([O-])C=C(C)c1ccc(C)cc1</chem>
Iodoform precipitate	Triiodomethane, or iodoform	<chem>IC(I)I</chem>

- **6.2.** The requested enantiomer is **(2R)-2-hydroxypropanal**, C[C@H](O)C=O. Its Fischer projection has CHO at the top, CH₃ at the bottom, OH on the right and H on the left. It is **D-lactaldehyde**.

Solution

6.1

Identification of the functional groups and ozonolysis fragments.

The degree of unsaturation of **A** is

$$\text{DBE} = \frac{2(12) + 2 - 16}{2} = 5.$$

The absorptions at 1580 and 1500 cm⁻¹ indicate an aromatic ring, accounting for four degrees of unsaturation. The remaining degree corresponds to the alkene cleaved by ozonolysis.

The strong absorption at 3000–3500 cm⁻¹ indicates an alcohol group. The negative 2,4-D test is consistent with the absence of an aldehyde or ketone. Oxidation followed by a positive iodoform reaction identifies a secondary methyl alcohol unit:



Both ozonolysis products contain a carbonyl group, as shown by their positive 2,4-D tests. **B**, which does not reduce Tollens reagent, is a ketone. Its only oxygen atom is therefore its carbonyl oxygen, so the original alcohol group must be in **C**.

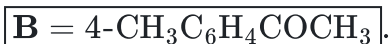
With only three carbon atoms, **C** must accommodate both the retained $-\text{CH}(\text{OH})\text{CH}_3$ unit and a carbonyl carbon. Consequently,



which is lactaldehyde and gives the observed Tollens reaction.

Identification of B and its nitration products.

The aromatic ketone **B** has formula $C_9H_{10}O$. The existence of only two distinct aromatic mononitration products identifies a para-disubstituted ring with different substituents. Hence **B** is 4-methylacetophenone:

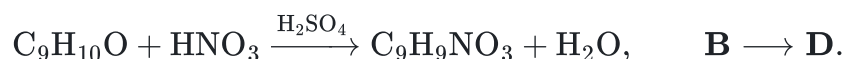


Number the ring carbon bearing the acetyl group as position 1; the methyl group is at position 4. The remaining positions form two equivalent pairs:

- Positions 3 and 5 are **meta to acetyl and ortho to methyl**.
- Positions 2 and 6 are **ortho to acetyl and meta to methyl**.

The acetyl group directs electrophilic substitution meta, while methyl directs ortho/para. Both therefore favor positions 3 and 5, giving **D**, 1-(4-methyl-3-nitrophenyl)ethan-1-one. Substitution at position 2 or 6 would give **E**.

The balanced nitration equation is



Reconstruction of A.

Reverse the ozonolysis by joining the carbonyl carbons of **B** and **C** with a double bond, removing their carbonyl oxygens. This gives

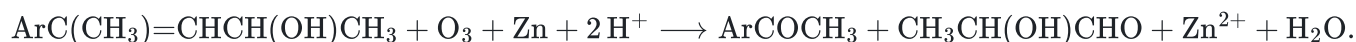


The alcohol carbon is stereogenic. Its two possible configurations are represented by:

- **(2R)-4-(4-methylphenyl)pent-3-en-2-ol**: C[C@H](O)C=C(C)c1ccc(C)cc1
- **(2S)-4-(4-methylphenyl)pent-3-en-2-ol**: C[C@@H](O)C=C(C)c1ccc(C)cc1

The information does not select either absolute configuration or either alkene geometry.

For the reaction equations below, let **Ar** denote the **4-methylphenyl group**, $4\text{-CH}_3\text{C}_6\text{H}_4$. A balanced net equation for ozonolysis with reductive work-up is

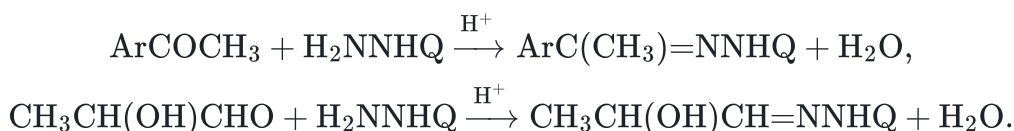


Thus the two organic products are **B** and **C**, respectively.

The 2,4-D reactions.

The reagent is **2,4-dinitrophenylhydrazine**, NNc1ccc([N+](=O)[O-])cc1[N+](=O)[O-].

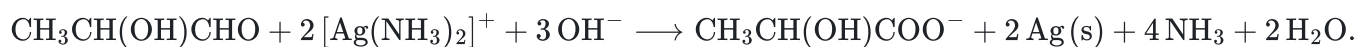
Let **Q** denote its **2,4-dinitrophenyl group**, $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$, so that the reagent is written H_2NNHQ . The carbonyl compounds undergo acid-catalyzed condensation:



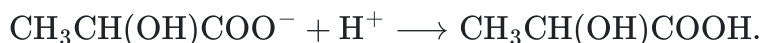
These give the two precipitated hydrazones listed in the Answers. Their imine geometries are not specified by the problem. **A** has no carbonyl group and therefore does not undergo this condensation.

Tollens oxidation and formation of F.

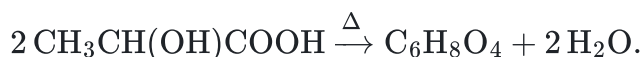
Tollens reagent oxidizes the aldehyde group of **C** to carboxylate while depositing silver:



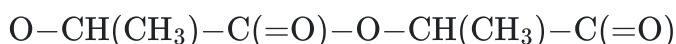
The organic product is **lactate**. Acidification gives **lactic acid**:



Two lactic acid molecules then undergo double esterification on heating:



The product is **F**, lactide. To draw it, make a six-membered ring with the sequence

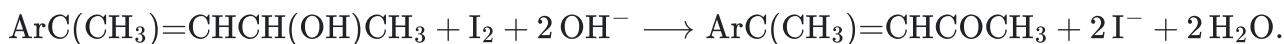
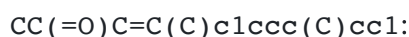


and connect the final carbonyl carbon back to the first oxygen.

This cyclic diester has two carbonyl groups and one ring, consistent with its three degrees of unsaturation. Both alcohol groups and both carboxylic acid groups have been consumed, explaining the absence of an O–H absorption above 3100 cm^{-1} . The problem does not establish its absolute stereochemistry.

The iodoform reaction of A.

First, the secondary alcohol is oxidized to **4-(4-methylphenyl)pent-3-en-2-one**,



The resulting methyl ketone undergoes the haloform reaction:



The overall equation in sodium hydroxide is therefore



The yellow precipitate is **iodoform**; the other organic product is **sodium 3-(4-methylphenyl)but-2-enoate**.

The small coproducts appearing in these equations are water O, zinc(II) ion [Zn+2], silver [Ag], ammonia N, iodide [I-], and sodium iodide [Na+] . [I-].

6.2

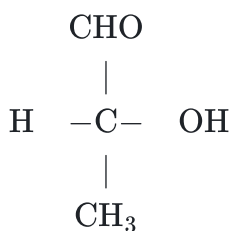
For lactaldehyde, the CIP priorities at the stereogenic carbon are



Oxygen has the highest priority. Between the two carbon substituents, the aldehyde carbon is treated as attached to O, O, H, whereas the methyl carbon is attached to H, H, H. Thus aldehyde outranks methyl.

To depict **R-lactaldehyde**, direct the bond to hydrogen away from the viewer. Viewed along that direction, place OH at 12 o'clock, CHO at 4 o'clock and CH₃ at 8 o'clock. The order 1 → 2 → 3 is clockwise.

Its Fischer projection is



The horizontal bonds point toward the viewer; the vertical bonds point away. The projected sequence 1 → 2 → 3 is counterclockwise, but hydrogen is toward the viewer, so reversal gives **R**.

With the aldehyde at the top and the hydroxyl group on the right, this is the **D configuration**:

(R)-lactaldehyde is D-lactaldehyde

with stereochemical SMILES C[C@H](O)C=O.

The solution was checked against the official solution.

Problem 7: Ideal-gas expansion and a refrigeration cycle

7.1 When an ideal, monatomic gas expands reversibly from a volume V_1 to a volume V_2 , a work

$$w = - \int_{V_1}^{V_2} p dV$$

is performed on the system by the surroundings. In this equation, w is the work and p is the pressure of the gas.

Determine the performed work when one mole ideal gas expands isothermally from $V_1 = 1.00 \text{ dm}^3$ to $V_2 = 20.0 \text{ dm}^3$ at the temperature $T = 300.0 \text{ K}$.

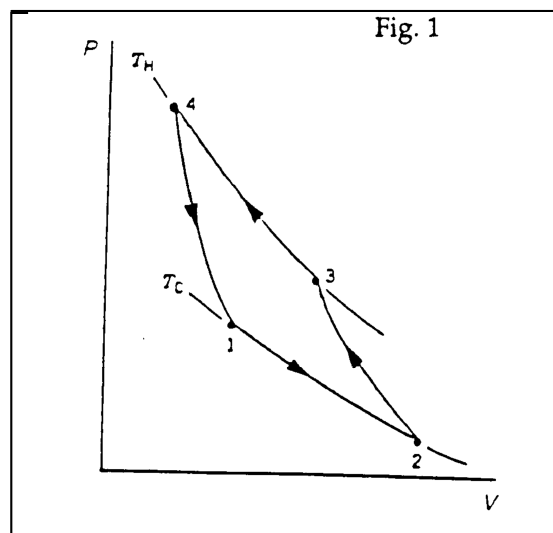
Given: The gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

7.2 Determine how much heat must be added to the gas during the process given under 7.1.

7.3 The gas will perform less work in an adiabatic expansion than in an isothermal expansion. Is this because the adiabatic expansion is characterized by (check the square you think is most important).

1	The volume of the gas is constant
2	The expansion is always irreversible
3	No heat is supplied to the gas

7.4 The cyclic process shown schematically in Figure 1 shows the four steps in a refrigeration system with an ideal gas as working medium. Identify the isothermal and adiabatic steps in the process. Here, T_H and T_C represent high and low temperature, respectively. Specify for each step whether it is adiabatic or isothermal.



Official English text of the problem.

Answers

- **7.1:** $w = -7.47 \text{ kJ}$, using the stated convention for work done on the gas.
- **7.2:** $q = +7.47 \text{ kJ}$; this heat must be added to the gas.
- **7.3:** Check **square 3: "No heat is supplied to the gas."**
- **7.4:** $1 \rightarrow 2$: isothermal expansion at T_C ; $2 \rightarrow 3$: adiabatic compression; $3 \rightarrow 4$: isothermal compression at T_H ; $4 \rightarrow 1$: adiabatic expansion.

Solution

7.1

For an ideal gas,

$$pV = nRT.$$

Since the expansion is isothermal, T is constant, so

$$w = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \left(\frac{V_2}{V_1} \right).$$

Substituting the given quantities,

$$\begin{aligned} w &= -(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300.0 \text{ K}) \ln \left(\frac{20.0 \text{ dm}^3}{1.00 \text{ dm}^3} \right) \\ &= -7471.96 \text{ J} \\ &= \boxed{-7.47 \text{ kJ}}. \end{aligned}$$

The volume ratio is dimensionless. The negative sign means that the gas does work on its surroundings: the work delivered by the gas is 7.47 kJ .

7.2

With work defined as work done **on** the gas, the first law is

$$\Delta U = q + w.$$

For a monatomic ideal gas,

$$\Delta U = \frac{3}{2}nR\Delta T.$$

The temperature remains constant, so $\Delta U = 0$. Therefore,

$$q = -w = \boxed{+7.47 \text{ kJ}}.$$

Thus 7.47 kJ of heat must enter the gas to replace the energy transferred to the surroundings as work.

7.3

The correct choice is **3: No heat is supplied to the gas.**

In an adiabatic process, $q = 0$. During expansion the gas does work, so its internal energy decreases:

$$\Delta U = w < 0.$$

Consequently, its temperature falls. Comparing reversible expansions from the same initial state to the same final volume, the adiabatic gas therefore has a lower pressure at each intermediate volume than the isothermal gas.

For a monatomic ideal gas, $\gamma = C_p/C_V = 5/3$. Hence, for $V > V_1$,

$$p_{\text{ad}} = p_1 \left(\frac{V_1}{V} \right)^{5/3} < p_1 \left(\frac{V_1}{V} \right) = p_{\text{iso}}.$$

The area under the pressure–volume curve, $\int p dV$, is consequently smaller for the adiabatic expansion, so the gas delivers less work.

Option 1 is incorrect because the volume increases during expansion. Option 2 is incorrect because an adiabatic expansion can be reversible.

7.4

The lower curve through states 1 and 2 is the isotherm at T_C ; the upper curve through states 3 and 4 is the isotherm at T_H . The connecting branches are adiabatic.

Step	Identification	Reasoning
1 $\rightarrow$ 2	Isothermal expansion at T_C	Volume increases along the cold isotherm. The gas absorbs heat while doing work, maintaining constant temperature.
2 $\rightarrow$ 3	Adiabatic compression	Volume decreases without heat exchange. Work done on the gas raises its temperature from T_C to T_H .
3 $\rightarrow$ 4	Isothermal compression at T_H	Volume decreases along the hot isotherm. The gas releases heat to maintain constant temperature.
4 $\rightarrow$ 1	Adiabatic expansion	Volume increases without heat exchange. The gas does work and cools from T_H to T_C .

These identifications also agree with the slopes: isotherms obey $pV = \text{constant}$, whereas reversible adiabats obey $pV^{5/3} = \text{constant}$ and are steeper at a given state.

The solution was checked against the official solution.

Problem 8: Radioactive decay of uranium and ruthenium-97

Avogadro's Number: $6.022 \cdot 10^{23}$

8.1 An atom of ^{238}U disintegrates by a series of α -decays and β^- -decays until it becomes ^{206}Pb , which is stable.

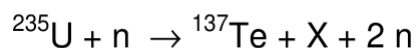
i) How many α -decays and how many β^- -decays does an atom starting as ^{238}U undergo before it becomes stable?

ii) One of the following ten nuclides is formed from a series of disintegrations starting at ^{238}U . Which one ?

^{235}U , ^{234}U , ^{228}Ac , ^{224}Ra , ^{224}Rn , ^{220}Rn , ^{215}Po , ^{212}Po , ^{212}Pb , ^{211}Pb .

8.2 In a thermal neutron-induced fission process, ^{235}U reacts with a neutron and breaks up into energetic fragments and (normally) 2-3 new neutrons.

We consider one single fission event:



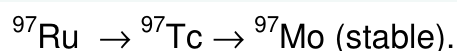
Identify the fragment X.

8.3 The half-life of ^{238}U is 4.5×10^9 years, the half-life of ^{235}U is 7.0×10^8 years. Natural uranium consists of 99.28 % ^{238}U and 0.72 % ^{235}U .

i) Calculate the ratio in natural U between the disintegration rates of these two uranium isotopes.

ii) A mineral contains 50 weight percent uranium. Calculate the disintegration rate of ^{238}U in 1.0 kg of this mineral.

8.4 We have the following radioactive sequence:



Half-lives: ^{97}Ru : 2.7 days; ^{97}Tc : 2.6×10^6 years

At $t = 0$ a radioactive source containing only ^{97}Ru has a disintegration rate of 1.0×10^9 Bq.

i) What is the total disintegration rate of the source at $t = 6.0$ days?

ii) What is the total disintegration rate of the source at $t = 6000$ years?

Official English text of the problem.

Answers

- **8.1(i):** 8 α -decays and 6 β^- -decays.
- **8.1(ii):** Uranium-234, ^{234}U .
- **8.2:** Zirconium-97, $^{97}_{40}\text{Zr}$.
- **8.3(i):** $R_{238}/R_{235} \approx 21$, or approximately 21 : 1.
- **8.3(ii):** $R_{238} = 6.1 \times 10^6$ Bq.

- **8.4(i):** $R_{\text{total}}(6.0 \text{ days}) = 2.1 \times 10^8 \text{ Bq}$.
- **8.4(ii):** $R_{\text{total}}(6000 \text{ years}) = 2.8 \text{ Bq}$.

Solution

8.1(i)

An α -decay reduces the mass number by 4 and the atomic number by 2. A β^- -decay leaves the mass number unchanged and increases the atomic number by 1.

Thus the number of α -decays is

$$n_{\alpha} = \frac{238 - 206}{4} = \boxed{8}.$$

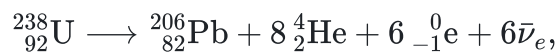
Uranium has atomic number 92, and lead has atomic number 82. Therefore,

$$92 - 2n_{\alpha} + n_{\beta^-} = 82,$$

giving

$$n_{\beta^-} = 82 - 92 + 16 = \boxed{6}.$$

The net nuclear equation is



where $\bar{\nu}_e$ denotes the electron antineutrino emitted in each β^- -decay.

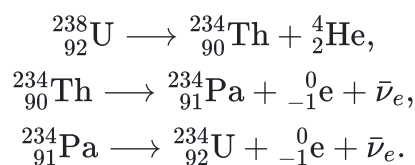
8.1(ii)

After any number k of α -decays, the mass number must be

$$A = 238 - 4k.$$

Since β^- -decay does not change A , every member of this decay series has $A \equiv 2 \pmod{4}$. Among the ten listed nuclides, only ${}^{234}\text{U}$ satisfies this condition.

It is produced through the sequence



Hence the answer is **uranium-234**, ${}^{234}\text{U}$.

8.2

Conservation of mass number gives

$$235 + 1 = 137 + A_X + 2,$$

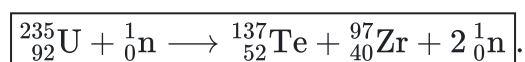
so

$$A_X = 97.$$

Tellurium has atomic number 52. Conservation of nuclear charge gives

$$92 = 52 + Z_X, \quad Z_X = 40.$$

Element 40 is zirconium. Thus X is **zirconium-97**, and the balanced fission equation is



8.3(i)

The disintegration rate, or activity, of a radioactive isotope is

$$R = \lambda N = \frac{\ln 2}{T_{1/2}} N.$$

Taking the given isotopic abundances as atom fractions,

$$\frac{R_{238}}{R_{235}} = \frac{N_{238}}{N_{235}} \frac{T_{1/2,235}}{T_{1/2,238}} = \frac{0.9928}{0.0072} \frac{7.0 \times 10^8}{4.5 \times 10^9} = 21.45.$$

Therefore,

$$\boxed{R_{238} : R_{235} \approx 21 : 1}.$$

8.3(ii)

The uranium mass in the mineral is

$$m_U = (1.0 \text{ kg})(0.50) = 0.50 \text{ kg} = 500 \text{ g}.$$

Approximating isotopic molar masses by their mass numbers, the mean molar mass of this uranium is

$$\overline{M}_U = [0.9928(238) + 0.0072(235)] \text{ g mol}^{-1} = 237.9784 \text{ g mol}^{-1}.$$

The number of ^{238}U atoms is consequently

$$N_{238} = 0.9928 \frac{500 \text{ g}}{237.9784 \text{ g mol}^{-1}} (6.022 \times 10^{23} \text{ mol}^{-1}) = 1.2561 \times 10^{24}.$$

Using $1 \text{ year} = 365 \times 24 \times 3600 \text{ s}$,

$$R_{238} = \frac{(\ln 2)(1.2561 \times 10^{24})}{(4.5 \times 10^9)(365)(24)(3600) \text{ s}} = 6.1354 \times 10^6 \text{ s}^{-1}.$$

Since $1 \text{ Bq} = 1 \text{ s}^{-1}$,

$$\boxed{R_{238} = 6.1 \times 10^6 \text{ Bq}}.$$

This is the activity of ^{238}U itself.

8.4 — decay equations used in both parts

Let λ_R and λ_T be the decay constants of ^{97}Ru and ^{97}Tc , respectively:

$$\lambda_R = \frac{\ln 2}{2.7(86400) \text{ s}} = 2.9713 \times 10^{-6} \text{ s}^{-1},$$

$$\lambda_T = \frac{\ln 2}{(2.6 \times 10^6)(365)(86400) \text{ s}} = 8.4537 \times 10^{-15} \text{ s}^{-1}.$$

The initial activity $R_0 = 1.0 \times 10^9 \text{ Bq}$ corresponds to

$$N_0 = \frac{R_0}{\lambda_R} = 3.3655 \times 10^{14}$$

ruthenium atoms.

The parent and daughter populations obey

$$\frac{dN_R}{dt} = -\lambda_R N_R, \quad \frac{dN_T}{dt} = \lambda_R N_R - \lambda_T N_T.$$

With $N_R(0) = N_0$ and $N_T(0) = 0$, their activities are

$$R_R(t) = R_0 e^{-\lambda_R t},$$

$$R_T(t) = R_0 \frac{\lambda_T}{\lambda_R - \lambda_T} (e^{-\lambda_T t} - e^{-\lambda_R t}).$$

Because ^{97}Mo is stable,

$$R_{\text{total}}(t) = R_R(t) + R_T(t).$$

8.4(i)

After 6.0 days, the ruthenium activity is

$$R_R = (1.0 \times 10^9) 2^{-6.0/2.7} = 2.1431 \times 10^8 \text{ Bq}.$$

The daughter activity from the expression above is only

$$R_T = 2.2354 \text{ Bq}.$$

It is negligible at the precision of the supplied data. Thus

$$\boxed{R_{\text{total}}(6.0 \text{ days}) = 2.1 \times 10^8 \text{ Bq}}.$$

8.4(ii)

After 6000 years, essentially all the original ruthenium has decayed. Since its decay took only a few days, the technetium population is, to excellent accuracy,

$$N_T(t) \simeq N_0 2^{-t/T_{1/2,T}}.$$

Its surviving fraction is

$$2^{-6000/(2.6 \times 10^6)} = 0.99840.$$

Therefore,

$$\begin{aligned} R_{\text{total}} &\simeq \lambda_T N_0 2^{-6000/(2.6 \times 10^6)} \\ &= (8.4537 \times 10^{-15} \text{ s}^{-1})(3.3655 \times 10^{14})(0.99840) \\ &= 2.8406 \text{ Bq}. \end{aligned}$$

Hence

$$\boxed{R_{\text{total}}(6000 \text{ years}) = 2.8 \text{ Bq}}.$$

The solution was checked against the official solution.