

IChO 2010

Theory problems and solutions · Tokyo, Japan · 9 theory problems with complete solutions

eulersolve.org/icho/2010/

Problem 1: Lord Rayleigh and the discovery of argon

In 1894, Lord Rayleigh reported that the mass of chemically prepared nitrogen was different from that of nitrogen extracted from the atmosphere, as shown in Tables 1 and 2. Later, this difference was attributed to the presence of argon in *atmospheric nitrogen*. The masses of gases were measured by using a glass vessel with a known volume under atmospheric pressure ($1.013 \cdot 10^5 \text{ Pa}$).

Table 1. Mass of *Chemical Nitrogen* in the Vessel

From nitric oxide	2.3001 g
From nitrous oxide	2.2990 g
From ammonium nitrite purified at a red heat	2.2987 g
From urea	2.2985 g
From ammonium nitrite purified in the cold	2.2987 g
Mean	2.2990 g

Table 2. Mass of *Atmospheric Nitrogen* in the Vessel

O ₂ was removed by hot copper (1892)	2.3103 g
O ₂ was removed by hot iron (1893)	2.3100 g
O ₂ was removed by ferrous hydrate (1894)	2.3102 g
Mean	2.3102 g

1.1 Calculate the volume $V \text{ [m}^3\text{]}$ of the vessel used by Rayleigh from the mean mass of *chemical nitrogen*, which must have been pure nitrogen. Assume that the measurements were carried out at a temperature of 15.0°C .

1.2 Estimate the mole fraction x of argon in Rayleigh's *atmospheric nitrogen*, by assuming that argon and nitrogen were the only constituents. Use the mean masses of the *atmospheric* and *chemical nitrogen* for the calculation.

Ramsay and Clève discovered helium in cleveite (a mineral consisting of uranium oxide and oxides of lead, thorium, and rare earths; an impure variety of uraninite) independently and virtually simultaneously in 1895. The gas extracted from the rock showed a unique spectroscopic line at around 588 nm (indicated by D₃ in Figure 1), which was first observed in the spectrum of solar prominence during a total eclipse in 1868, near the well-known D₁ and D₂ lines of sodium.

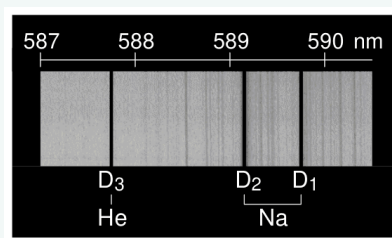


Figure 1. Spectral lines around 588 nm

1.3 Calculate the energy $E \text{ [J]}$ of a photon with the wavelength of the D₃ line of helium shown in Figure 1.

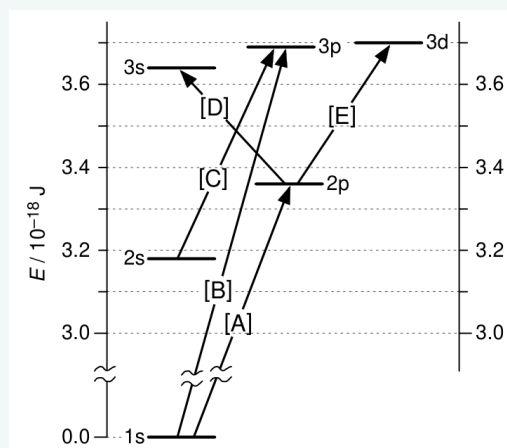


Figure 2. Energy diagram of atomic orbitals of helium when an electron resides in the 1s orbital.

Figure 2 shows an energy diagram of the atomic orbitals of helium. The arrows indicate the "allowed" transitions according to the spectroscopic principle.

1.4 Identify the transition relevant to the D_3 line of helium among the transitions [A] to [E] indicated in Figure 2. Mark one of the following:

☐ [A] ☐ [B] ☐ [C] ☐ [D] ☐ [E]

1.5 Which equation explains the occurrence of helium in cleveite among [A] to [D] below? Mark one.

- ☐ [A] $^{238}\text{U} \rightarrow ^{234}\text{Th} + \alpha$
- ☐ [B] $\text{UHe}_2 \rightarrow \text{U} + 2 \text{He}$
- ☐ [C] $^{240}\text{U} \rightarrow ^{240}\text{Np} + \beta^-$
- ☐ [D] $^{235}\text{U} + \text{n} \rightarrow ^{95}\text{Y} + ^{139}\text{I} + 2 \text{n}$

Argon is also found in minerals such as *malacon*.

1.6 Which equation explains the occurrence of argon in rocks among [A] to [D] below? Mark one.

- ☐ [A] $\text{ArF}_2 \rightarrow \text{Ar} + \text{F}_2$
- ☐ [B] $\text{ArXe} \rightarrow \text{Ar} + \text{Xe}$
- ☐ [C] $^{40}\text{K} \rightarrow ^{40}\text{Ar} + \varepsilon/\beta^+$ (electron capture / positron emission)
- ☐ [D] $^{126}\text{I} \rightarrow ^{126}\text{Ar} + \beta^-$

One of the strongest evidences for the monoatomicity of argon and helium is the ratio of the heat capacity under constant pressure to that at constant volume, $\gamma = C_p/C_v$, which is exactly $5/3$ (1.67 ± 0.01) for a monoatomic gas. The ratio was derived from the measurement of speed of sound v_s by using the following equation, where f and λ are the frequency and wavelength of the sound, and R , T , and M denote the molar gas constant, absolute temperature, and molar mass, respectively.

$$v_s = f\lambda = \sqrt{\frac{\gamma RT}{M}}$$

For an unknown gas sample, the wavelength of the sound was measured to be $\lambda = 0.116 \text{ m}$ at a frequency of $f = 3520 \text{ Hz}$ ($\text{Hz} = \text{s}^{-1}$) and temperature of 15.0°C and under atmospheric pressure ($1.013 \cdot 10^5 \text{ Pa}$). The density ρ of the gas for these conditions was measured to be $0.850 \pm 0.005 \text{ kg m}^{-3}$.

1.7 Calculate the molar mass M [kg mol^{-1}] of this gas.

1.8 Calculate the heat capacity ratio γ for this gas sample.

1.9 Which is this gas? Choose and mark among [A] to [D] .

- ☐ [A] HCl
- ☐ [B] HF
- ☐ [C] Ne
- ☐ [D] Ar

Official English text of the problem.

Answers

- 1.1: $V = 1.94 \times 10^{-3} \text{ m}^3$.
- 1.2: $x = 0.0114$, corresponding to 1.14 mol% argon.
- 1.3: $E = 3.38 \times 10^{-19} \text{ J}$ per photon.
- 1.4: [E], the $2p \leftrightarrow 3d$ transition; emission is $3d \rightarrow 2p$.
- 1.5: [A], alpha decay of uranium-238.
- 1.6: [C], conversion of potassium-40 into argon-40.
- 1.7: $M = 2.01 \times 10^{-2} \text{ kg mol}^{-1}$.
- 1.8: $\gamma = 1.40$.
- 1.9: [B], hydrogen fluoride, HF , SMILES [H] F .

Solution

The calculations use the ideal-gas model and

$$T = 273.15 + 15.0 = 288.15 \text{ K}.$$

The problem does not print the physical constants; standard values used here are

$$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}, \quad h = 6.6261 \times 10^{-34} \text{ J s}, \quad c = 2.9979 \times 10^8 \text{ m s}^{-1}.$$

1.1

Pure nitrogen is molecular nitrogen, N_2 , SMILES N#N, with molar mass 28.02 g mol^{-1} . Its amount in the vessel is

$$n = \frac{m}{M} = \frac{2.2990 \text{ g}}{28.02 \text{ g mol}^{-1}} = 0.08205 \text{ mol}.$$

From $pV = nRT$,

$$V = \frac{nRT}{p} = \frac{(0.08205)(8.3145)(288.15)}{1.013 \times 10^5} \text{ m}^3 = \boxed{1.94 \times 10^{-3} \text{ m}^3}.$$

1.2

Argon, Ar , SMILES [Ar], has molar mass 39.95 g mol^{-1} .

At the same pressure, temperature, and vessel volume, the pure nitrogen and the mixture contain the same total amount of gas. If x is the argon mole fraction, the mixture's mean molar mass is

$$\overline{M} = (1 - x)M(\text{N}_2) + xM(\text{Ar}).$$

Consequently,

$$\frac{m_{\text{atmospheric}}}{m_{\text{chemical}}} = \frac{\overline{M}}{M(\text{N}_2)} = 1 + x \frac{M(\text{Ar}) - M(\text{N}_2)}{M(\text{N}_2)}.$$

Solving,

$$x = \left(\frac{2.3102}{2.2990} - 1 \right) \frac{28.02}{39.95 - 28.02} = 0.011442 \dots$$

and therefore

$$\boxed{x = 0.0114 \quad \text{or} \quad 1.14 \text{ mol}\%}.$$

This is the argon fraction in Rayleigh's oxygen-removed atmospheric sample.

1.3

The helium line—helium, He , SMILES [He]—has wavelength approximately 588 nm . Its photon energy is

$$E = h\nu = \frac{hc}{\lambda}.$$

Thus,

$$E = \frac{(6.6261 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m s}^{-1})}{588 \times 10^{-9} \text{ m}} = \boxed{3.38 \times 10^{-19} \text{ J}}.$$

Reading the line more closely as approximately 587.7 nm gives the same result to three significant figures.

1.4

The photon energy must equal the separation between the two levels:

$$\Delta E = 3.38 \times 10^{-19} \text{ J} = 0.338 \times 10^{-18} \text{ J}.$$

From Figure 2, the $2p$ and $3d$ levels lie at approximately $3.36 \times 10^{-18} \text{ J}$ and $3.70 \times 10^{-18} \text{ J}$, respectively. Their separation is

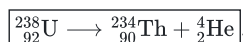
$$\Delta E \approx (3.70 - 3.36) \times 10^{-18} = 3.4 \times 10^{-19} \text{ J},$$

which matches the photon energy.

Therefore, **mark [E]**. The upward arrow represents absorption, $2p \rightarrow 3d$; emission of the same spectral line corresponds to $3d \rightarrow 2p$. The other electron remains in the $1s$ orbital.

1.5

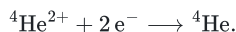
Uranium-238 undergoes alpha decay:



Both nucleon number and nuclear charge are conserved:

$$238 = 234 + 4, \quad 92 = 90 + 2.$$

The emitted alpha particle is a helium-4 nucleus, ${}^4\text{He}^{2+}$, SMILES [4He+2]. After slowing down, it acquires two electrons:

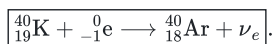


This produces neutral helium-4, SMILES [4He], which can accumulate in the mineral.

Therefore, **mark [A]**. SMILES identifies the chemical species; the nuclear transformation is specified by the isotope equation.

1.6

Potassium-40 can form argon-40 by electron capture:



Here ν_e is an electron neutrino. The mass number remains 40, while the nuclear charge decreases from 19 to 18.

The positron-emission alternative included in option [C] is



Both processes produce argon-40, ${}^{40}\text{Ar}$, SMILES [40Ar], which can remain trapped in rocks. Therefore, **mark [C]**.

1.7

Combining the ideal-gas equation with $n = m/M$ and $\rho = m/V$,

$$pV = \frac{m}{M}RT \implies M = \frac{\rho RT}{p}.$$

Therefore,

$$M = \frac{(0.850 \text{ kg m}^{-3})(8.3145 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1})(288.15 \text{ K})}{1.013 \times 10^5 \text{ Pa}} = \boxed{2.01 \times 10^{-2} \text{ kg mol}^{-1}}.$$

Propagating only the stated density uncertainty,

$$\delta M = M \frac{\delta \rho}{\rho} \approx 1.2 \times 10^{-4} \text{ kg mol}^{-1}.$$

Thus a result displaying that uncertainty is

$$M = (0.02010 \pm 0.00012) \text{ kg mol}^{-1}.$$

1.8

The measured speed of sound is

$$v_s = f\lambda = (3520 \text{ s}^{-1})(0.116 \text{ m}) = 408.32 \text{ m s}^{-1}.$$

Rearranging the supplied relation and substituting $M = \rho RT/p$,

$$\gamma = \frac{Mv_s^2}{RT} = \frac{\rho v_s^2}{p}.$$

Hence,

$$\gamma = \frac{(0.850)(408.32)^2}{1.013 \times 10^5} = 1.39898 \dots = \boxed{1.40}.$$

The density uncertainty alone gives

$$\delta \gamma = \gamma \frac{0.005}{0.850} \approx 0.0082,$$

or approximately $\gamma = 1.399 \pm 0.008$.

1.9

The measured molar mass is approximately 20.1 g mol^{-1} . This excludes hydrogen chloride, HCl , SMILES [HCl], and argon, Ar , SMILES [Ar], whose molar masses are approximately 36.46 and 39.95 g mol^{-1} , respectively.

Both hydrogen fluoride, HF , SMILES [HF], with $M \approx 20.01 \text{ g mol}^{-1}$, and neon, Ne , SMILES [Ne], with $M \approx 20.18 \text{ g mol}^{-1}$, are compatible with the molar-mass measurement.

The heat-capacity ratio distinguishes them. A monatomic ideal gas such as neon has

$$C_V = \frac{3}{2}R, \quad C_p = \frac{5}{2}R, \quad \gamma = \frac{5}{3} \approx 1.67.$$

A diatomic ideal gas with active translational and rotational motion, but negligible vibrational excitation, has

$$C_V = \frac{5}{2}R, \quad C_p = \frac{7}{2}R, \quad \gamma = \frac{7}{5} = 1.40.$$

The measured ratio agrees with the diatomic gas. Therefore, **mark [B]: hydrogen fluoride, HF , SMILES [HF]**.

The solution was checked against the official solution.

Problem 2: Crystal structure of alkali metal halides

Crystal structure of alkali metal halide

In crystals of ionic compounds, cations are generally arranged in the interstices of the closest packed lattice of anions. The structure of an ionic crystal such as sodium chloride becomes stable when the cations are in contact with the nearest anions.

2.1 In the crystal of sodium chloride, both Na^+ and Cl^- ions form a face-centred cubic lattice. Give the numbers of Na^+ and Cl^- ions in a unit cell and the coordination numbers of Na^+ and Cl^- ions in sodium chloride crystal.

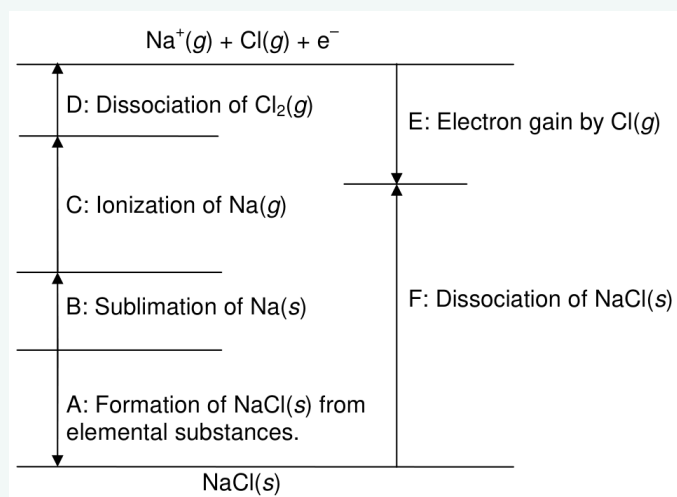
2.2 The ionic radii of Na^+ and Cl^- ions in the crystal of sodium chloride are 0.102 nm and 0.181 nm, respectively.

Calculate the density [kg m^{-3}] of the sodium chloride crystal.

Born-Haber cycle and lattice enthalpy

In ionic inorganic compounds such as sodium chloride, the heat of lattice formation from gaseous ions is very high, and the contribution of the change in entropy is small. Therefore, the lattice formation enthalpy is estimated from enthalpy data by using a Born-Haber cycle.

2.3 The figure below shows the Born-Haber cycle of NaCl . The labels "g" and "s" represent "gas" and "solid" states, respectively. Show chemical equations in the A and F steps.



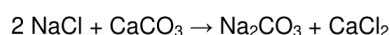
2.4 Calculate the enthalpy of the lattice formation of NaCl [kJ mol^{-1}] by using the following enthalpy data of the respective steps in the above Born-Haber cycle.

Formation of NaCl(s)	Sublimation of Na(s)	Ionization of Na(g)	Dissociation of $\text{Cl}_2(\text{g})$	Electron gain by Cl(g)
-411 kJ mol^{-1}	109 kJ mol^{-1}	496 kJ mol^{-1}	242 kJ mol^{-1}	-349 kJ mol^{-1}

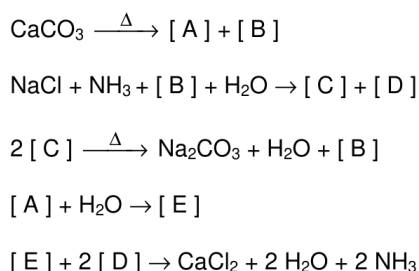
Synthesis of sodium carbonate by the ammonia-soda process (Solvay process)

Sodium carbonate (anhydrous soda ash) is a raw material in the manufacture of glass, medicaments, alkaline detergents, etc.

2.5 The total chemical reaction in the ammonia-soda process is represented as follows:



This reaction between sodium chloride and calcium carbonate does not proceed directly. The process comprises the following five reactions involving ammonia:



where Δ represents applying heat treatment. Insert the chemical formulas of the appropriate compounds instead of [A] – [E] in the above reactions.

Official English text of the problem.

Answers

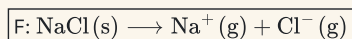
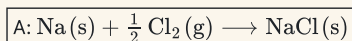
SMILES for salts below specify their constituent ions. They do not encode the extended crystal lattice or its coordination geometry.

- 2.1:** The conventional cubic unit cell contains **4 sodium ions**, Na^+ , [Na+], and **4 chloride ions**, Cl^- , [Cl-]. Both ions have coordination number **6**, with **octahedral coordination**.

- **2.2:** For sodium chloride, NaCl, [Na⁺] · [Cl⁻],

$$\rho = 2.14 \times 10^3 \text{ kg m}^{-3}.$$

- **2.3:**



Sodium is represented by [Na]; chlorine (dichlorine) by ClCl. The sodium SMILES does not describe the metallic lattice.

- **2.4:**

$$\Delta H_{\text{lattice formation}} = -788 \text{ kJ mol}^{-1}.$$

The reverse process, step F, has $\Delta H_F = +788 \text{ kJ mol}^{-1}$.

- **2.5:**

A: calcium oxide, CaO, [Ca+2] · [O-2]

B: carbon dioxide, CO₂, O=C=O

C: sodium hydrogen carbonate (sodium bicarbonate), NaHCO₃, [Na+] · OC(=O) [O-]

D: ammonium chloride, NH₄Cl, [NH₄+] · [Cl-]

E: calcium hydroxide, Ca(OH)₂, [Ca+2] · [OH-] · [OH-]

Solution

2.1

Choose the conventional cubic cell with chloride ions at its corners and face centres. A corner ion is shared by eight cells, and a face-centred ion is shared by two cells. Therefore,

$$N_{\text{Cl}^-} = 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = \boxed{4}.$$

Sodium ions occupy all the octahedral sites of this chloride lattice: the twelve edge centres and the body centre. An edge-centred ion is shared by four cells, while the body-centred ion belongs entirely to one cell:

$$N_{\text{Na}^+} = 12 \left(\frac{1}{4} \right) + 1 = \boxed{4}.$$

Each sodium ion has six nearest chloride neighbours, situated along the positive and negative directions of three mutually perpendicular axes. These neighbours form an octahedron around it. The same description applies to the six sodium neighbours of each chloride ion.

Thus,

$$\boxed{\text{CN}(\text{Na}^+) = \text{CN}(\text{Cl}^-) = 6}.$$

2.2

Let the cubic cell edge be a . Along an edge, a corner chloride ion touches the sodium ion at the edge centre. Their separation is $a/2$, so

$$\frac{a}{2} = r_{\text{Na}^+} + r_{\text{Cl}^-}.$$

Consequently,

$$a = 2(0.102 + 0.181) \text{ nm} = 0.566 \text{ nm} = 5.66 \times 10^{-10} \text{ m}.$$

The cell volume is

$$V_{\text{cell}} = a^3 = (5.66 \times 10^{-10} \text{ m})^3 = 1.81321496 \times 10^{-28} \text{ m}^3.$$

There are four formula units of sodium chloride per cell, hence

$$m_{\text{cell}} = \frac{4M(\text{NaCl})}{N_A}.$$

The problem does not list molar masses or Avogadro's constant. Using the standard values

$$M(\text{NaCl}) = (22.99 + 35.45) \text{ g mol}^{-1} = 58.44 \times 10^{-3} \text{ kg mol}^{-1},$$

$$N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1},$$

gives

$$m_{\text{cell}} = \frac{4(58.44 \times 10^{-3})}{6.02214076 \times 10^{23}} = 3.88168 \times 10^{-25} \text{ kg}.$$

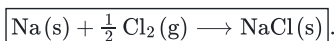
Therefore,

$$\rho = \frac{m_{\text{cell}}}{V_{\text{cell}}} = \frac{3.88168 \times 10^{-25}}{1.81321496 \times 10^{-28}} \text{ kg m}^{-3},$$

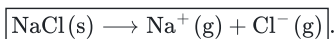
$$\boxed{\rho = 2.14 \times 10^3 \text{ kg m}^{-3}}.$$

2.3

Step A forms one mole of solid sodium chloride from its elements in their standard states: solid sodium and gaseous chlorine. Since chlorine is diatomic, half a mole is required:



The upward arrow F represents dissociation of the solid into separated gaseous ions:



Both equations conserve atoms and charge. Step F is the reverse of lattice formation.

2.4

Write the alternative route from the elements to solid sodium chloride. The atomic chlorine intermediate, Cl(g) , has SMILES `[Cl]`.

Step	Reaction	Enthalpy contribution per mole of NaCl, kJ mol^{-1}
B: sublimation	$\text{Na(s)} \longrightarrow \text{Na(g)}$	+109
C: ionization	$\text{Na(g)} \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$	+496
D: chlorine dissociation	$\frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{Cl(g)}$	$+\frac{242}{2} = +121$
E: electron gain	$\text{Cl(g)} + \text{e}^- \longrightarrow \text{Cl}^-(\text{g})$	-349
Lattice formation	$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{NaCl(s)}$	$\Delta H_{\text{lattice formation}}$

The chlorine dissociation value is halved because the stated 242 kJ mol^{-1} applies to dissociation of one mole of Cl_2 , producing two moles of chlorine atoms.

Adding the reactions cancels the gaseous intermediates and the electron, leaving the formation reaction in step A. Hess's law therefore gives

$$-411 = 109 + 496 + \frac{242}{2} - 349 + \Delta H_{\text{lattice formation}}.$$

Thus,

$$\Delta H_{\text{lattice formation}} = -411 - (109 + 496 + 121 - 349) = -411 - 377,$$

$$\Delta H_{\text{lattice formation}} = -788 \text{ kJ mol}^{-1}.$$

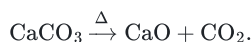
The negative sign indicates that forming the ionic lattice releases heat.

2.5

The additional species appearing in the completed reactions are:

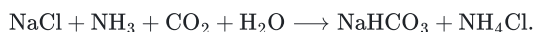
Name	Formula	SMILES
Calcium carbonate	CaCO_3	<code>[Ca+2].[O-]C(=O)[O-]</code>
Ammonia	NH_3	<code>N</code>
Water	H_2O	<code>O</code>
Sodium carbonate	Na_2CO_3	<code>[Na+].[Na+].[O-]C(=O)[O-]</code>
Calcium chloride	CaCl_2	<code>[Ca+2].[Cl-].[Cl-]</code>

Heating calcium carbonate produces calcium oxide and carbon dioxide:



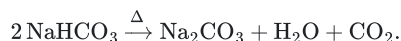
Therefore, **A** is CaO and **B** is CO_2 .

Carbon dioxide reacts with ammonia and water in the sodium chloride solution. Sodium hydrogen carbonate precipitates because of its relatively low solubility under the process conditions; ammonium chloride remains in solution:



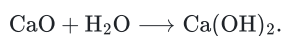
Thus, **C** is NaHCO_3 and **D** is NH_4Cl .

Heating sodium hydrogen carbonate produces sodium carbonate, water, and carbon dioxide:



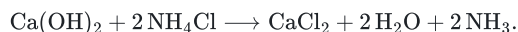
This confirms C and also regenerates some of the carbon dioxide used in the preceding reaction.

Calcium oxide reacts with water to form calcium hydroxide:

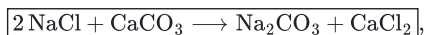


Hence, **E** is Ca(OH)_2 .

Finally, the basic calcium hydroxide regenerates ammonia from ammonium chloride:



To verify the overall stoichiometry, take the carbonation reaction twice and each of the other four reactions once. Cancelling the intermediates, ammonia, carbon dioxide, and water gives



as required.

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 3: Chemical oxygen demand

The chemical oxygen demand (COD) refers to the amount of oxidizable substance, such as organic compounds, in a sample solution, and it is used as an indication of water quality in seas, lakes, and marshes. For example, the COD of service water is kept below 1 mg dm^{-3} . The COD (mg dm^{-3}) is represented by mass of O_2 (mg) which accepts the same amount of electrons which would be accepted by the strong oxidizing agent when 1 dm^3 of a sample solution is treated with it. An example of the operation is presented below.

Analytical Operation

A sample solution with a volume of 1.00 dm^3 was acidified with a sufficient amount of sulphuric acid, and chloride ions were removed by the addition of silver nitrate solution. A volume of $1.00 \cdot 10^{-1} \text{ dm}^3$ of potassium permanganate solution ($c = 5.00 \cdot 10^{-3} \text{ mol dm}^{-3}$) was added to the sample solution, and the mixture was heated for 30 min. Further, a volume of $1.00 \cdot 10^{-1} \text{ dm}^3$ of disodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$ or $\text{NaOOC}-\text{COONa}$) standard solution ($c = 1.25 \cdot 10^{-2} \text{ mol dm}^{-3}$) was added, and the mixture was stirred well. Oxalate ions that remained unreacted were titrated with potassium permanganate solution ($c = 5.00 \cdot 10^{-3} \text{ mol dm}^{-3}$). A volume of $3.00 \cdot 10^{-2} \text{ dm}^3$ of the solution was used for the titration.

3.1 Give the equation of the redox reaction of potassium permanganate and disodium oxalate.

3.2 Calculate the mass of O_2 (in mg) that will oxidize the same number of moles of oxidizable substance as $1.00 \cdot 10^{-3} \text{ dm}^3$ of potassium permanganate solution with a concentration of $5.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ does.

3.3 From the following choices, select the most appropriate reason for the removal of chloride ions:

[A] Some of the chloride ions react with potassium permanganate, resulting in an error in COD.

[B] Some of the chloride ions react with disodium oxalate, resulting in an error in COD.

[C] Some of the chloride ions react with organic compounds in the sample solution, resulting in an error in COD.

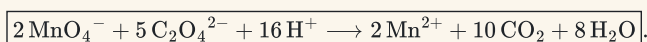
[D] A colour is developed during titration, resulting in an error in COD.

3.4 Calculate the COD (mg dm^{-3}) of the sample solution described in the analytical operation above.

Official English text of the problem.

Answers

- 3.1** The balanced net ionic equation is



Species names and SMILES are given in the solution.

- 3.2** 0.200 mg of dioxygen, O_2 , SMILES $\text{O}=\text{O}$.
- 3.3** [A]. Chloride consumes permanganate, increasing the apparent COD.
- 3.4** $\text{COD} = 6.00 \text{ mg dm}^{-3}$.

Solution

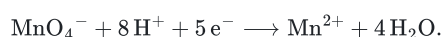
3.1 — Permanganate–oxalate reaction

The species participating in the net ionic reaction are:

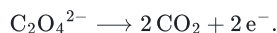
Formula	Name	SMILES
MnO_4^-	Permanganate ion	[O-][Mn](=O)(=O)=O
$\text{C}_2\text{O}_4^{2-}$	Oxalate ion	[O-]C(=O)C(=O)[O-]
H^+	Hydrogen ion (proton)	[H+]
Mn^{2+}	Manganese(II) ion	[Mn+2]
CO_2	Carbon dioxide	O=C=O
H_2O	Water	O

The permanganate SMILES is a formal bond representation; the ion has tetrahedral geometry.

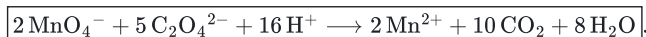
In acidic solution, manganese is reduced from oxidation state $+7$ to $+2$, accepting five electrons:



Each carbon atom in oxalate is oxidized from $+3$ to $+4$, so each oxalate ion releases two electrons:



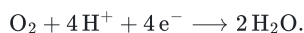
Multiplying the first half-reaction by 2 and the second by 5 cancels ten electrons:



Thus, 2 mol of permanganate react with 5 mol of oxalate.

3.2 — Oxygen equivalent of the permanganate solution

Dioxygen, O_2 ($\text{O}=\text{O}$), accepts four electrons per molecule when reduced to water:



The specified volume contains

$$n(\text{MnO}_4^-) = (5.00 \cdot 10^{-3} \text{ mol dm}^{-3})(1.00 \cdot 10^{-3} \text{ dm}^3) = 5.00 \cdot 10^{-6} \text{ mol}.$$

Since each permanganate ion accepts five electrons, the equivalent amount of oxygen is

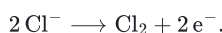
$$n(\text{O}_2) = \frac{5}{4}n(\text{MnO}_4^-) = 6.25 \cdot 10^{-6} \text{ mol}.$$

Using $M(\text{O}_2) = 32.0 \text{ g mol}^{-1}$,

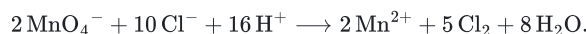
$$m(\text{O}_2) = (6.25 \cdot 10^{-6} \text{ mol})(32.0 \text{ g mol}^{-1})(10^3 \text{ mg g}^{-1}) = \boxed{0.200 \text{ mg}}.$$

3.3 — Reason for removing chloride

Chloride ions, Cl^- ($[\text{Cl}^-]$), can be oxidized by acidified permanganate to chlorine, Cl_2 (ClCl):

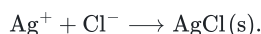


Combining this with permanganate reduction gives



This reaction consumes some of the permanganate. That consumption would be included in the measured oxygen demand and would therefore increase the apparent COD. The correct choice is **[A]**.

Silver nitrate supplies silver(I) ions, Ag^+ ($[\text{Ag}^+]$), which remove chloride by precipitating silver chloride, AgCl ($[\text{Ag}^+] \cdot [\text{Cl}^-]$):



The silver chloride SMILES specifies its ionic composition; it does not encode the solid's crystal lattice.

3.4 — COD of the sample

The initial amount of permanganate is

$$n_0(\text{MnO}_4^-) = (1.00 \cdot 10^{-1})(5.00 \cdot 10^{-3}) = 5.00 \cdot 10^{-4} \text{ mol}.$$

The amount of oxalate added after heating is

$$n_{\text{added}}(\text{C}_2\text{O}_4^{2-}) = (1.00 \cdot 10^{-1})(1.25 \cdot 10^{-2}) = 1.25 \cdot 10^{-3} \text{ mol}.$$

This oxalate first consumes the permanganate remaining after oxidation of the sample. The excess oxalate is then measured by titration.

The final titration uses

$$n_{\text{titration}}(\text{MnO}_4^-) = (3.00 \cdot 10^{-2})(5.00 \cdot 10^{-3}) = 1.50 \cdot 10^{-4} \text{ mol}.$$

From the 2 : 5 permanganate-to-oxalate ratio, the excess oxalate is

$$n_{\text{excess}}(\text{C}_2\text{O}_4^{2-}) = \frac{5}{2}(1.50 \cdot 10^{-4}) = 3.75 \cdot 10^{-4} \text{ mol}.$$

Therefore, the oxalate that reacted with the residual permanganate was

$$n_{\text{reacted}}(\text{C}_2\text{O}_4^{2-}) = 1.25 \cdot 10^{-3} - 3.75 \cdot 10^{-4} = 8.75 \cdot 10^{-4} \text{ mol}.$$

The permanganate remaining after oxidation of the sample was consequently

$$n_{\text{remaining}}(\text{MnO}_4^-) = \frac{2}{5}(8.75 \cdot 10^{-4}) = 3.50 \cdot 10^{-4} \text{ mol}.$$

Hence, the sample consumed

$$n_{\text{sample}}(\text{MnO}_4^-) = 5.00 \cdot 10^{-4} - 3.50 \cdot 10^{-4} = 1.50 \cdot 10^{-4} \text{ mol}.$$

The equivalent oxygen mass is

$$\begin{aligned} m(\text{O}_2) &= \frac{5}{4}(1.50 \cdot 10^{-4} \text{ mol})(32.0 \text{ g mol}^{-1})(10^3 \text{ mg g}^{-1}) \\ &= 6.00 \text{ mg}. \end{aligned}$$

COD is expressed per volume of the **original sample**, which was 1.00 dm^3 :

$$\boxed{\text{COD} = \frac{6.00 \text{ mg}}{1.00 \text{ dm}^3} = 6.00 \text{ mg dm}^{-3}}.$$

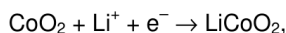
As a check, the added oxalate has exactly the electron capacity of the initial permanganate. Thus, the final 30.0 mL titration corresponds directly to the sample's demand. From part 3.2, each 1.00 mL corresponds to 0.200 mg of oxygen, giving $30.0 \times 0.200 = 6.00$ mg.

The solution was checked against the official solution.

Problem 4: The lithium-ion battery

The rechargeable lithium ion battery has been developed in Japan.

The standard electromotive force of the battery is 3.70 V. Assume that the half-reaction at the cathode is



and the half-reaction at the anode is



4.1 Write the total reaction equation of the battery and calculate the value of the standard Gibbs energy of the reaction [kJ mol^{-1}].

The battery cell is constructed using LiCoO_2 and graphite (C) as the electrode materials.

4.2 Calculate the mass of the anode in the completely charged state and that in completely discharged state if 10.00 g of LiCoO_2 and 10.00 g of graphite (C) are present initially.

4.3 Calculate the maximum energy generated per mass of the lithium ion battery cell [kJ kg^{-1}]. Assume that the correct ratio for complete reaction between the cathode and anode materials is used and the sum of the mass of electrodes is 50.0 % of the total mass of the battery cell. In comparison, the energy density of lead-acid batteries used for vehicles is about 200 kJ kg^{-1} .

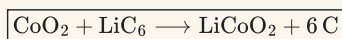
Because an aqueous solution cannot be used as an electrolyte, an organic solution is used in the lithium ion battery cell.

4.4 Give the chemical formula of the gas generated if water is present in the electrolyte.

Official English text of the problem.

Answers

• **4.1**



$$\Delta_r G^\circ = -357 \text{ kJ mol}^{-1}$$

• **4.2** Completely charged anode: 10.71 g . Completely discharged anode: 10.00 g .

• **4.3**

$$1.05 \times 10^3 \text{ kJ kg}^{-1}$$

• **4.4** Hydrogen gas (dihydrogen), H_2 ; SMILES: $[\text{H}][\text{H}]$.

Solution

For numerical evaluation, use

$$F = 96\,485 \text{ C mol}^{-1},$$

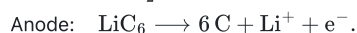
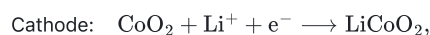
and atomic molar masses

$$M_{\text{Li}} = 6.94, \quad M_{\text{Co}} = 58.93, \quad M_{\text{O}} = 16.00, \quad M_{\text{C}} = 12.01 \quad (\text{g mol}^{-1}).$$

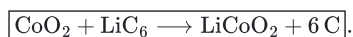
The electrode materials—cobalt(IV) oxide, CoO_2 ; lithium cobalt(III) oxide, LiCoO_2 ; lithiated graphite, LiC_6 ; and graphite, C—are extended solids. They have no discrete molecular structures to represent by molecular SMILES.

4.1

The given discharge half-reactions are



Adding them cancels the lithium ions, Li^+ (SMILES: $[\text{Li}^+]$), and electrons:



One mole of electrons is transferred per mole of reaction as written, so $n = 1$. Hence

$$\begin{aligned}
 \Delta_r G^\circ &= -nFE^\circ \\
 &= -(1)(96\,485\text{ C mol}^{-1})(3.70\text{ V}) \\
 &= -3.569945 \times 10^5\text{ J mol}^{-1} \\
 &= \boxed{-357\text{ kJ mol}^{-1}}.
 \end{aligned}$$

The negative sign corresponds to spontaneous discharge under standard conditions.

4.2

Charging reverses the overall discharge reaction:



Thus lithium moves from the positive electrode into graphite. The amount available from the initial lithium cobalt oxide is

$$\begin{aligned}
 M(\text{LiCoO}_2) &= 6.94 + 58.93 + 2(16.00) = 97.87\text{ g mol}^{-1}, \\
 n_{\text{Li,available}} &= \frac{10.00\text{ g}}{97.87\text{ g mol}^{-1}} = 0.102176\text{ mol}.
 \end{aligned}$$

The graphite can accommodate one lithium atom per six carbon atoms:

$$n_{\text{Li,capacity}} = \frac{10.00\text{ g}}{6(12.01\text{ g mol}^{-1})} = 0.138773\text{ mol}.$$

Since the graphite capacity exceeds the available lithium, all the lithium can transfer, with some graphite remaining unintercalated. The transferred mass is

$$m_{\text{Li}} = (0.102176\text{ mol})(6.94\text{ g mol}^{-1}) = 0.709104\text{ g}.$$

Therefore, the completely charged anode has mass

$$m_{\text{charged}} = 10.00 + 0.709104 = \boxed{10.71\text{ g}}.$$

Complete discharge transfers this lithium back to the cobalt oxide electrode, leaving the original graphite:

$$\boxed{m_{\text{discharged}} = 10.00\text{ g}}.$$

4.3

For maximum energy per mass, use the stoichiometric electrode ratio. One mole of reaction requires one mole of LiCoO_2 and six moles of carbon in the discharged state. Their combined mass is

$$\begin{aligned}
 m_{\text{electrodes}} &= 97.87 + 6(12.01) \\
 &= 169.93\text{ g}.
 \end{aligned}$$

Charging redistributes lithium between the electrodes, so their combined mass is unchanged.

Because the electrodes constitute 50.0% of the cell mass,

$$m_{\text{cell}} = \frac{169.93\text{ g}}{0.500} = 339.86\text{ g} = 0.33986\text{ kg}.$$

The maximum electrical energy delivered per mole of reaction is

$$W_{\text{max}} = -\Delta_r G^\circ = 356.9945\text{ kJ}.$$

Consequently,

$$\begin{aligned}
 \frac{W_{\text{max}}}{m_{\text{cell}}} &= \frac{356.9945\text{ kJ}}{0.33986\text{ kg}} \\
 &= \boxed{1.05 \times 10^3\text{ kJ kg}^{-1}}.
 \end{aligned}$$

This is approximately 5.25 times the stated lead-acid battery energy density.

4.4

The lithiated graphite electrode is strongly reducing. Water, H_2O (SMILES: `O`), can accept electrons and form hydrogen gas and hydroxide ions, OH^- (SMILES: `[OH-]`):



Combining this with oxidation of lithiated graphite gives



Thus the gas is **hydrogen (dihydrogen)**:



with SMILES `[H][H]`.

The solution was checked against the official solution.

Problem 5: Photoelectron spectroscopy

When an atom X absorbs radiation with a photon energy greater than the ionization energy of the atom, the atom is ionized to generate an ion X^+ and the electron (called a photoelectron) is ejected at the same time. In this event, the energy is conserved as shown in Figure 1, that is, Photon energy ($h\nu$) = ionization energy (IE) of X + kinetic energy of photoelectron.

When a molecule, for example, H_2 , absorbs short-wavelength light, the photoelectron is ejected and an H_2^+ ion with a variety of vibrational states is produced. A photoelectron spectrum is a plot of the number of photoelectrons as a function of the kinetic energy of the photoelectrons. Figure 2 shows a typical photoelectron spectrum when H_2 in the lowest vibrational level is irradiated by monochromatic light of 21.2 eV. No photoelectrons are detected above 6.0 eV. (eV is a unit of energy and 1.0 eV is equal to $1.6 \cdot 10^{-19}$ J.)

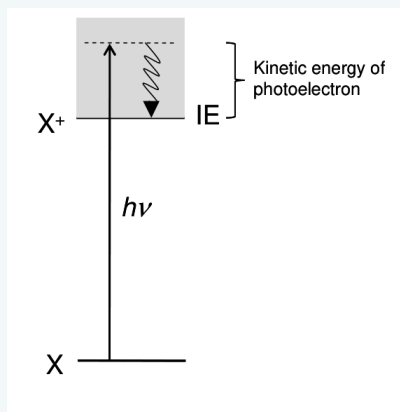


Figure 1. Schematic diagram of photoelectron spectroscopy.

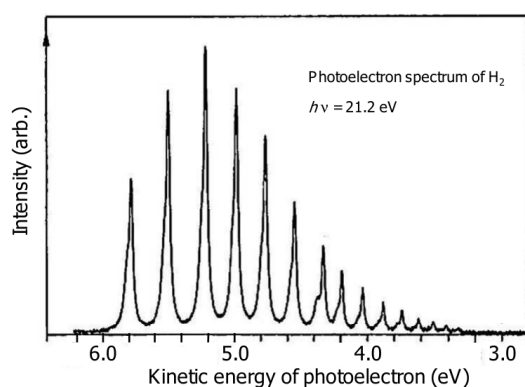


Figure 2.
Photoelectron spectrum of H_2 .
The energy of the incident light is 21.2 eV.

Figure 2. Photoelectron spectrum of H_2 . The energy of the incident light is 21.2 eV.

5.1 a) Determine the energy difference ΔE_{A1} (eV) between H_2 ($v = 0$) and H_2^+ ($v_{\text{ion}} = 0$) to the first decimal place. v and v_{ion} denote the vibrational quantum numbers of H_2 and H_2^+ , respectively.

b) Determine the energy difference ΔE_{A2} (eV) between H_2^+ ($v_{\text{ion}} = 0$) and H_2^+ ($v_{\text{ion}} = 3$) to the first decimal place.

The electronic energy levels E_n^H of a hydrogen atom are given by the equation

$$E_n^H = -\frac{Ry}{n^2} \quad (n = 1, 2, 3 \dots)$$

Here n is a principal quantum number, and Ry is a constant with dimensions of energy. The energy from $n = 1$ to $n = 2$ of the hydrogen atom is 10.2 eV.

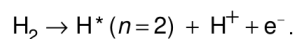
5.2 Calculate the ionization energy E_B (eV) of the hydrogen atom to the first decimal place.

The energy threshold for the generation of two electronically excited hydrogen atoms H^* ($n = 2$) from H_2 ($v = 0$) has been derived to be 24.9 eV by an experiment.

5.3 Determine the bond energy E_C (eV) of H_2 to the first decimal place.

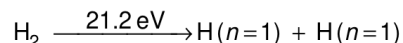
5.4 Considering an energy cycle, determine the bond energy E_D (eV) of H_2^+ to the first decimal place. If you were unable to determine the values for E_B and E_C , then use 15.0 eV and 5.0 eV for E_B and E_C , respectively.

5.5 Calculate the threshold energy E_E (eV) of the following dissociative ionization reaction to the first decimal place:



If you were unable to determine the values for E_B and E_C , then use 15.0 eV and 5.0 eV for E_B and E_C , respectively.

When H_2 absorbs monochromatic light of 21.2 eV, the following dissociation process occurs at the same time.



Two hydrogen atoms move in opposite directions with the same speed.

5.6 Calculate the speed u (m s^{-1}) of the hydrogen atoms generated in the above reaction. H_2 is assumed to be at rest. If you were unable to determine the value for E_C , then use 5.0 eV for E_C .

Official English text of the problem.

Answers

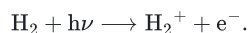
- **5.1 a)** $\Delta E_{A1} = 15.4 \text{ eV}$.
- **5.1 b)** $\Delta E_{A2} = 0.8 \text{ eV}$.
- **5.2** $E_B = 13.6 \text{ eV}$.
- **5.3** $E_C = 4.5 \text{ eV}$.
- **5.4** $E_D = 2.7 \text{ eV}$.
- **5.5** $E_E = 28.3 \text{ eV}$.
- **5.6** $u = 4.0 \times 10^4 \text{ m s}^{-1}$ for each atom, using $m_H \approx 1.67 \times 10^{-27} \text{ kg}$.

Solution

The species used below are molecular hydrogen (dihydrogen), H_2 , [H][H]; the hydrogen molecular ion (dihydrogen radical cation), H_2^+ , [H][H+]; atomic hydrogen, H, [H]; and the hydrogen ion (proton), H^+ , [H+]. For H_2^+ , the SMILES is a connectivity and charge shorthand: it does not faithfully represent the delocalized one-electron bond, whose bond order is 1/2. These SMILES also do not specify vibrational states or atomic electronic excitation.

5.1 a)

Photoionization produces an ion and a photoelectron:



The initial molecule has $v = 0$. If the ion is produced in vibrational level j , conservation of energy gives

$$h\nu = \Delta E_{A1} + \epsilon_j + K_j,$$

where ϵ_j is the ion's vibrational energy above $v_{\text{ion}} = 0$, and K_j is the photoelectron kinetic energy.

The greatest photoelectron kinetic energy therefore corresponds to the lowest final ionic energy, $v_{\text{ion}} = 0$. The kinetic-energy axis decreases from left to right, so this is the leftmost peak, centered at approximately 5.8 eV.

Thus,

$$\Delta E_{A1} = 21.2 - 5.8 = 15.4 \text{ eV}.$$

5.1 b)

Successive peaks toward lower kinetic energy correspond to successively higher ionic vibrational levels. Counting the first peak as $v_{\text{ion}} = 0$, the fourth peak represents $v_{\text{ion}} = 3$. Its kinetic energy is approximately 5.0 eV.

Because the photon energy and initial molecular state are identical, the increase in ionic energy equals the decrease in photoelectron kinetic energy:

$$\begin{aligned} \Delta E_{A2} &= E_{\text{ion}}(3) - E_{\text{ion}}(0) \\ &= K_0 - K_3 \\ &= 5.8 - 5.0. \end{aligned}$$

Therefore,

$$\Delta E_{A2} = 0.8 \text{ eV}.$$

5.2

For the given electronic energy levels,

$$E_2^{\text{H}} - E_1^{\text{H}} = -\frac{Ry}{4} - (-Ry) \\ = \frac{3}{4}Ry = 10.2 \text{ eV}.$$

Hence,

$$Ry = \frac{4}{3}(10.2) = 13.6 \text{ eV}.$$

Ionization of ground-state atomic hydrogen is

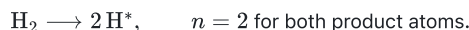


The free-electron limit is $n \rightarrow \infty$, for which $E_{\infty}^{\text{H}} = 0$. Therefore,

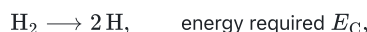
$$E_{\text{B}} = E_{\infty}^{\text{H}} - E_1^{\text{H}} = Ry = 13.6 \text{ eV}.$$

5.3

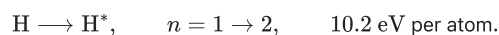
The experimentally specified process is



It can be resolved into dissociation to ground-state atoms,



followed by excitation of both atoms:



Consequently,

$$24.9 \text{ eV} = E_{\text{C}} + 2(10.2 \text{ eV}),$$

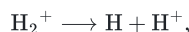
and

$$E_{\text{C}} = 24.9 - 20.4 = 4.5 \text{ eV}.$$

This is the dissociation energy from the molecular $v = 0$ level.

5.4

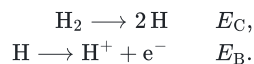
The required ionic dissociation is



with the ion initially in $v_{\text{ion}} = 0$ and the hydrogen atom produced in its ground electronic state.

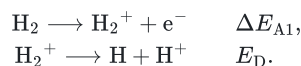
Consider two routes from ground-state H_2 to the same products, $\text{H} + \text{H}^+ + \text{e}^-$.

The first route dissociates the molecule and then ionizes one atom:



Its total energy requirement is $E_{\text{C}} + E_{\text{B}}$.

The second route ionizes the molecule and then dissociates the molecular ion:



Conservation of energy around the cycle requires

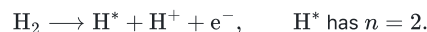
$$E_{\text{C}} + E_{\text{B}} = \Delta E_{\text{A1}} + E_{\text{D}}.$$

Thus,

$$E_{\text{D}} = 4.5 + 13.6 - 15.4 = 2.7 \text{ eV}.$$

5.5

The dissociative ionization reaction is



Starting from H_2 in $v = 0$, the required energy is the sum of:

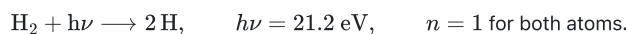
1. Dissociation into two ground-state hydrogen atoms: $E_{\text{C}} = 4.5 \text{ eV}$.
2. Excitation of one atom to $n = 2$: 10.2 eV .
3. Ionization of the other atom: $E_{\text{B}} = 13.6 \text{ eV}$.

At threshold, no excess energy is available for product kinetic energy. Therefore,

$$E_{\text{E}} = E_{\text{C}} + 10.2 + E_{\text{B}} = 4.5 + 10.2 + 13.6 = 28.3 \text{ eV}.$$

5.6

The photodissociation is



After supplying the bond dissociation energy, the remaining photon energy becomes the total kinetic energy:

$$K_{\text{total}} = h\nu - E_{\text{C}} = 21.2 - 4.5 = 16.7 \text{ eV}.$$

Both atoms have the same mass and speed, so

$$K_{\text{total}} = 2 \left(\frac{1}{2} m_{\text{H}} u^2 \right) = m_{\text{H}} u^2.$$

Using the stated conversion $1.0 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$, together with the standard hydrogen-atom mass $m_{\text{H}} \approx 1.67 \times 10^{-27} \text{ kg}$,

$$u = \sqrt{\frac{(16.7 \text{ eV})(1.6 \times 10^{-19} \text{ J eV}^{-1})}{1.67 \times 10^{-27} \text{ kg}}} \\ = \boxed{4.0 \times 10^4 \text{ m s}^{-1}}.$$

Each atom has this speed, with the two velocities pointing in opposite directions.

The solution was checked against the official solution.

Problem 6: Four isomers of C₈H₁₀O

Read the description of four kinds of isomeric organic compounds **A**, **B**, **C**, and **D**. All of them have the formula C₈H₁₀O and contain a benzene ring. Answer the questions that follow. If there are stereoisomers, give also their structural formulas.

- At room temperature, a piece of sodium metal was added (procedure 1) to A, B, and C in test tubes. The evolution of hydrogen gas was observed only in the case of **C**.
- When an iron(III) chloride aqueous solution was added to **C and D**, no coloration was observed in **C**, whereas **D** was coloured.
- **A** was oxidized when aqueous potassium permanganate was added to it and the mixture was heated. The acidification of the heated mixture and its isolation (procedure 2) afforded benzoic acid.
- Let's imagine that a hydrogen atom in the benzene ring is replaced by a chlorine atom (procedure 3). It is possible to obtain in this way four kinds of monochlorinated structural isomers from **B**, while only two kinds of such isomers can be obtained from **D**.
- Hydrogenation of the benzene ring in **C and D** using a catalyst gave saturated alcohol(s). It was found that the saturated alcohol(s) obtained from **C** has no stereogenic carbons while those obtained from **D** has stereogenic carbon(s).

6.1 Among all the isomeric organic compounds with a formula of C₈H₁₀O and having a benzene ring, give the structural formulas of all the isomers that do NOT yield hydrogen gas in the underlined procedure 1, in which a piece of sodium is added:

i) to the neat samples in the case of the liquid samples,

ii) to the concentrated solution of the samples in an aprotic solvent in the case of the solid samples.

6.2 Among all the isomeric organic compounds with a formula of C₈H₁₀O and having a benzene ring, give the structural formulas of all the isomers that yield benzoic acid in the underlined procedure 2.

6.3 Among all the isomeric organic compounds with a formula of C₈H₁₀O and having a benzene ring, give the structural formulas of all the isomers that could yield four different monochlorinated structural isomers when the underlined procedure 3 is performed.

6.4 Give the structural formulas of **A**, **B**, **C**, and **D**. When several isomers can be considered, give the structural formulas of all of them.

Official English text of the problem.

Answers

- **6.1 — Five ethers:**

Compound	SMILES
Ethoxybenzene (phenetole)	<chem>CCOc1ccccc1</chem>
(Methoxymethyl)benzene (benzyl methyl ether)	<chem>COCc1ccccc1</chem>
1-Methoxy-2-methylbenzene (2-methylanisole)	<chem>COc1ccccc1C</chem>
1-Methoxy-3-methylbenzene (3-methylanisole)	<chem>COc1cccc(C)c1</chem>
1-Methoxy-4-methylbenzene (4-methylanisole)	<chem>COc1ccc(C)cc1</chem>

- **6.2 — Three constitutional isomers, giving four structures when enantiomers are counted separately:**

Compound	SMILES
(Methoxymethyl)benzene	<chem>COCc1ccccc1</chem>
2-Phenylethan-1-ol	<chem>OCCc1ccccc1</chem>
(<i>R</i>)-1-Phenylethan-1-ol	<chem>C[C@H](O)c1ccccc1</chem>
(<i>S</i>)-1-Phenylethan-1-ol	<chem>C[C@@H](O)c1ccccc1</chem>

• **6.3 — Six constitutional isomers:**

Compound	SMILES
1-Methoxy-2-methylbenzene	<chem>COc1ccccc1C</chem>
1-Methoxy-3-methylbenzene	<chem>COc1cccc(C)c1</chem>
(2-Methylphenyl)methanol (2-methylbenzyl alcohol)	<chem>OCc1ccccc1C</chem>
(3-Methylphenyl)methanol (3-methylbenzyl alcohol)	<chem>OCc1cccc(C)c1</chem>
2-Ethylphenol	<chem>CCc1ccccc1O</chem>
3-Ethylphenol	<chem>CCc1cccc(O)c1</chem>

• **6.4 — All possible identifications:**

Label	Compound(s)	SMILES
A	(Methoxymethyl)benzene	<chem>COCc1ccccc1</chem>
B	1-Methoxy-2-methylbenzene; 1-methoxy-3-methylbenzene	<chem>COc1ccccc1C</chem> ; <chem>COc1cccc(C)c1</chem>
C	2-Phenylethan-1-ol; (4-methylphenyl)methanol	<chem>OCc1ccccc1</chem> ; <chem>OCc1ccc(C)cc1</chem>
D	2,6-Dimethylphenol; 3,5-dimethylphenol	<chem>Oc1c(C)cccc1C</chem> ; <chem>Oc1cc(C)cc(C)c1</chem>

Solution

The degree of unsaturation is

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

The benzene ring accounts for all four degrees of unsaturation. Consequently, there can be no additional ring, carbonyl group, or other multiple bond outside that ring. The oxygen must occur in an alcohol, a phenol, or an ether.

6.1

Alcohols and phenols contain an O—H bond and react with sodium, releasing hydrogen, $[\text{H}][\text{H}]$:



Here R may represent an alkyl or aryl group. Ethers lack this hydrogen and do not evolve hydrogen under the stated test conditions.

There are exactly five possible ethers:

1. With one substituent on the benzene ring, the two external carbon atoms can form either an ethoxy group or a methoxymethyl group. These give ethoxybenzene and (methoxymethyl)benzene.
2. With two substituents, the groups must be methyl and methoxy. Their three relative positions give the 2-, 3-, and 4-methylanisoles.

Their structures are listed in **Answers 6.1**. The use of neat samples or an aprotic solvent prevents a protic solvent from supplying hydrogen in the sodium test.

6.2

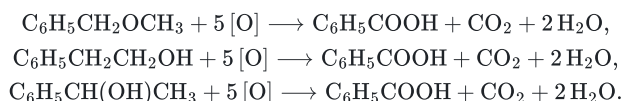
Hot aqueous permanganate oxidizes suitable carbon-containing side chains attached directly to a benzene ring to carboxyl groups. To obtain **unsubstituted benzoic acid**, the starting structure must have one such side chain and no other substituent that remains on the ring.

The three qualifying connectivities are:

- (Methoxymethyl)benzene;
- 2-phenylethan-1-ol;
- 1-phenylethan-1-ol.

The last compound has a carbon bonded to four different groups: hydrogen, hydroxy, methyl, and phenyl. Both its R and S enantiomers must therefore be included.

Balanced overall oxidation equations can be written as follows, using $[\text{O}]$ for an oxygen-atom equivalent supplied by the oxidant:



These overall equations represent the removed one-carbon fragment at its fully oxidized limit, carbon dioxide, $\text{O}=\text{C}=\text{O}$; water is O . The identification does not depend on isolating those coproducts.

Before acidification, the aromatic oxidation product is benzoate, $[\text{O}-]\text{C}(=\text{O})\text{c1ccccc1}$. Acidification gives benzoic acid, $\text{O}=\text{C}(\text{O})\text{c1ccccc1}$:



Other structures are excluded because:

- Ethoxybenzene has oxygen directly attached to the ring rather than a carbon side chain that can become the required carboxyl group.
- Methylanisoles retain a methoxy substituent during side-chain oxidation.

- Methylbenzyl alcohols have two oxidizable carbon side chains and give benzenedicarboxylic acids under exhaustive oxidation.
- Ethylphenols and dimethylphenols retain a phenolic hydroxy substituent during the relevant side-chain oxidation.

Thus none of these gives unsubstituted benzoic acid by the stated transformation.

6.3

This question counts constitutionally different positions for replacing a ring hydrogen by chlorine; it does not ask for the relative amounts produced in an actual chlorination.

A monosubstituted benzene has three classes of ring hydrogens: ortho, meta, and para. A ring with three or more substituents has at most three hydrogens available. Therefore, four monochlorinated structural isomers require a **disubstituted benzene**.

The possible pairs of substituents are:

Substituent pair	Structures giving four products
Methyl and methoxy	1,2- and 1,3-substitution
Methyl and hydroxymethyl	1,2- and 1,3-substitution
Ethyl and hydroxy	1,2- and 1,3-substitution

For two different substituents:

- In a **1,2-disubstituted** ring, all four remaining hydrogen positions are constitutionally distinct.
- In a **1,3-disubstituted** ring, all four remaining hydrogen positions are also constitutionally distinct.
- In a **1,4-disubstituted** ring, reflection symmetry makes positions 2 and 6 equivalent, and positions 3 and 5 equivalent. Only two products result.

This gives exactly the six structures in **Answers 6.3**.

6.4

Identification of A.

The negative sodium test restricts A to the five ethers in 6.1. Of these, only **(methoxymethyl)benzene** gives benzoic acid in procedure 2. Hence

A = (methoxymethyl)benzene

with SMILES COCc1ccccc1.

Identification of B.

B must also be an ether. Intersecting the five ethers from 6.1 with the six structures from 6.3 leaves:

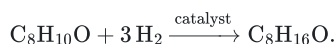
- **1-Methoxy-2-methylbenzene**, COC1CCCC1C;
- **1-methoxy-3-methylbenzene**, COC1CCCC(C)C1.

Both give four distinct ring-monochlorinated constitutional isomers.

Identification of C.

The positive sodium test indicates an O—H group. The negative iron(III) chloride test identifies C as a nonphenolic alcohol.

The possible nonphenolic alcohol connectivities are 2-phenylethan-1-ol, 1-phenylethan-1-ol, and the three methylbenzyl alcohols. Hydrogenation of their benzene rings consumes three equivalents of hydrogen:



The stereogenic-carbon test distinguishes them:

Candidate	Consequence of ring hydrogenation
2-Phenylethan-1-ol	No stereogenic carbon is formed.
Either enantiomer of 1-phenylethan-1-ol	The hydroxy-bearing side-chain carbon remains stereogenic.
2-Methylbenzyl alcohol	Both substituted ring carbons become stereogenic.
3-Methylbenzyl alcohol	Both substituted ring carbons become stereogenic.
4-Methylbenzyl alcohol	Neither substituted ring carbon has four different substituents.

For the ortho and meta methylbenzyl alcohols, the two paths around the saturated ring from a substituted carbon are different. In the para case, those paths are equivalent.

Thus C can be either:

- **2-Phenylethan-1-ol**, OCC1CCCC1, which gives **2-cyclohexylethan-1-ol**, OCCC1CCCC1;
- **(4-methylphenyl)methanol**, OC1ccc(C)cc1, which gives **(4-methylcyclohexyl)methanol**.

The latter saturated alcohol can have two relative configurations:

Saturated product	SMILES
cis-(4-Methylcyclohexyl)methanol	<chem>OC[C@H]1CC[C@@H](C)CC1</chem>
trans-(4-Methylcyclohexyl)methanol	<chem>OC[C@H]1CC[C@H](C)CC1</chem>

Here *cis* means the methyl and hydroxymethyl groups lie on the same face of the ring; *trans* means opposite faces. The cyclic @/@ notation encodes this relative stereochemistry. Such *cis/trans* isomerism does not require a carbon bearing four different substituents.

Identification of D.

The positive iron(III) chloride test indicates a phenol. Its colour arises from iron(III)–phenolate coordination. A schematic, balanced binding step is



Coordinated water is omitted here; the qualitative test does not specify one unique complex composition or coordination geometry.

The phenols with formula $\text{C}_8\text{H}_{10}\text{O}$ are ethylphenols and dimethylphenols. Exactly three have only two classes of ring hydrogen:

Phenol	Equivalent hydrogen-position classes, numbering the hydroxy-bearing carbon 1
4-Ethylphenol, <chem>CCc1ccc(O)cc1</chem>	{2, 6}, {3, 5}
2,6-Dimethylphenol, <chem>Oc1c(C)cccc1C</chem>	{3, 5}, {4}
3,5-Dimethylphenol, <chem>Oc1cc(C)cc(C)c1</chem>	{2, 6}, {4}

Hydrogenation eliminates **4-ethylphenol**: its saturated ring has 1,4-substitution and no carbon bearing four different substituents, just as in the para case considered for C.

The other two candidates satisfy the final condition:

- Hydrogenated **2,6-dimethylphenol** has stereogenic carbons at positions **2 and 6**.
- Hydrogenated **3,5-dimethylphenol** has stereogenic carbons at positions **3 and 5**.

At each methyl-bearing carbon, the four attachments are hydrogen, methyl, and two different paths around the ring. One path reaches the hydroxy-bearing carbon sooner than the other. This remains true for every possible relative configuration of the substituents.

Therefore,

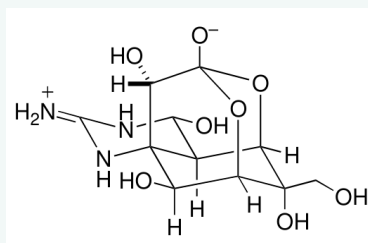
$$\boxed{\text{D} = \text{2,6-dimethylphenol or 3,5-dimethylphenol.}}$$

All parent structures identified as A–D are achiral. The only enantiomers required among the answers to 6.1–6.4 are the two forms of 1-phenylethan-1-ol in 6.2.

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

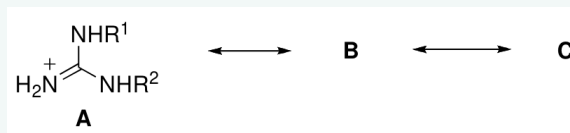
Problem 7: Tetrodotoxin

Certain varieties of puffer fish, *Fugu* in Japanese, are highly prized as foods in Japan. Since the viscera (especially ovaries and livers) of the fish contain a potent toxin (tetrodotoxin), food poisoning often results from its ingestion. Studies on tetrodotoxin (**1**) have been performed from the beginning of the 20th century. Its chemical structure was elucidated in 1964.



tetrodotoxin (**1**)

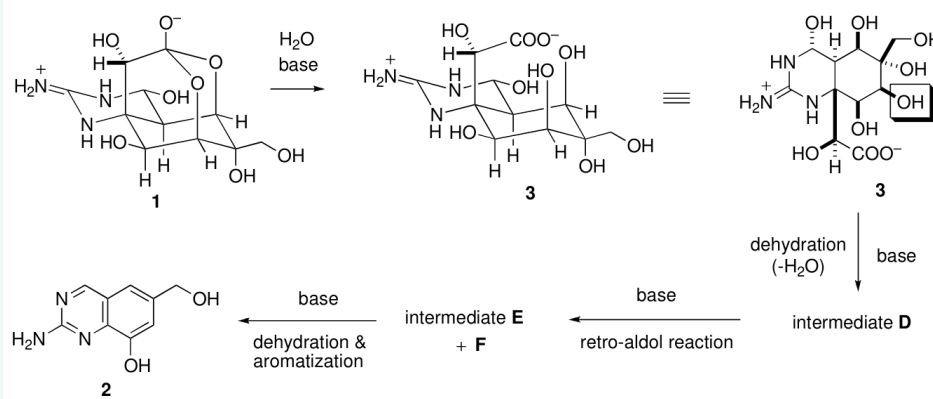
The guanidine group in tetrodotoxin exhibits strong basicity. The guanidinium ion resulting from protonation on the guanidine group is stabilized by the existence of the following resonance.



7.1 Draw two resonance structures **B** and **C**.

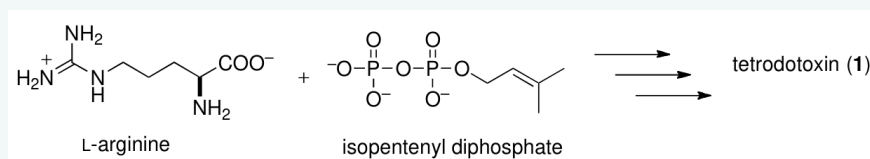
Many derivatization reactions were performed in structure studies of tetrodotoxin. Treatment of tetrodotoxin (**1**) (see reaction scheme 1) with ethanolic potassium hydroxide upon heating afforded quinazoline derivative **2**, which provided an insight into the nature of the fundamental skeleton of tetrodotoxin. The reaction mechanism can be described as follows. First, tetrodotoxin is hydrolyzed into carboxylate **3**. Then the hydroxyl group highlighted with a frame is eliminated by the base to give intermediate **D**. A retro-aldol reaction of **D** cleaves a carbon-carbon bond to provide intermediates **E** and **F**. Finally, dehydration and aromatization from **E** produce quinazoline derivative **2**.

7.2 Draw structures of the postulated intermediates **D**, **E**, and **F**.



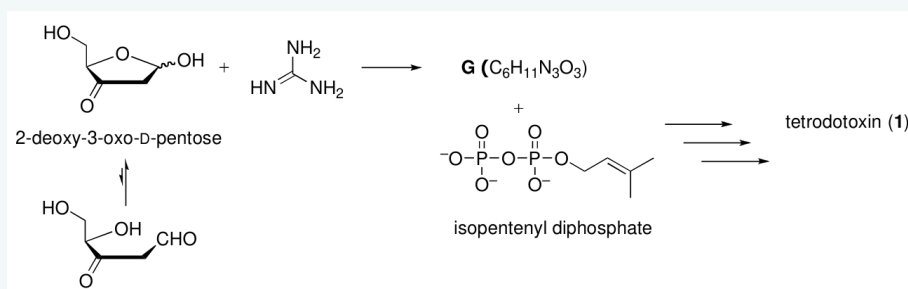
Reaction scheme 1

Although biosynthesis of tetrodotoxin still remains to be clarified, it is proposed that tetrodotoxin may be biologically synthesized from L-arginine and isopentenyl diphosphate.



7.3 Among the carbon atoms included in tetrodotoxin, circle all those that are expected to be of L-arginine origin.

In the 1990s, an alternative biosynthetic pathway of tetrodotoxin was proposed. Condensation between 2-deoxy-3-oxo-D-pentose and guanidine provides intermediate **G** with cyclic guanidine moiety (molecular formula $C_6H_{11}N_3O_3$). Tetrodotoxin may be biologically synthesized from intermediate **G** and isopentenyl diphosphate.



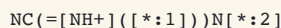
7.4 Draw a structure of the postulated intermediate **G** showing the stereochemistry.

Official English text of the problem.

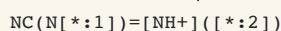
Answers

- 7.1** The two remaining contributors of the **disubstituted guanidinium ion** are:

B: double bond and positive charge on the nitrogen bearing R^1 :



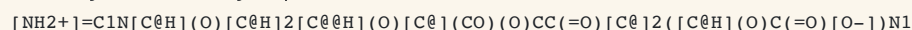
C: double bond and positive charge on the nitrogen bearing R^2 :



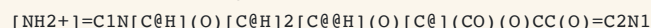
Here $[*:1]$ and $[*:2]$ represent R^1 and R^2 .

- 7.2** Using the atom numbering defined below:

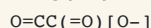
D — dehydrated carboxylate, C8-ketone tautomer:



E — retro-aldol product, C8-enol tautomer:

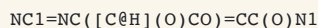


F — glyoxylate (2-oxoacetate), $OHC-COO^-$:



- 7.3** Circle **six carbons**: the guanidinium carbon **C2**, and **C4, C4a, C8a, C9, and C10**. These constitute the guanidinium carbon plus the five-carbon chain ending at the carboxylate carbon in **3**.

- **7.4 G — 2-amino-6-[(1S)-1,2-dihydroxyethyl]-3,4-dihydropyrimidin-4-ol**, a cyclic guanidine hemiaminal:



The side-chain stereocenter retains the sugar's configuration. The newly formed ring hemiaminal center is unspecified; draw its hydroxyl bond as wavy.

Solution

7.1 — Guanidinium resonance

In **A**, the positive charge is on the nitrogen of the exocyclic double bond. Either other nitrogen can donate its lone pair to the central carbon while the existing double-bond electrons move onto the initially positive nitrogen.

The resulting contributors are



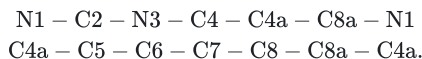
and



Thus, each contributor has one carbon–nitrogen double bond, with the positive charge on that double-bonded nitrogen. All atoms retain octets. Hydrogen atoms and substituents remain attached to the same nitrogens: these are resonance contributors, so no proton transfer occurs.

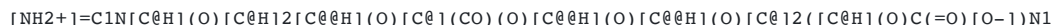
7.2 — Dehydration, retro-aldol cleavage, and aromatization

To identify bonds precisely, use the quinazoline numbering inherited from product **2**. The two fused rings follow these atom sequences:



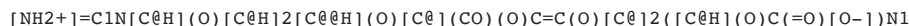
In carboxylate **3**, call the hydroxyl-bearing side-chain carbon attached to C8a **C9**, its carboxylate carbon **C10**, and the hydroxymethyl carbon attached to C6 **C11**.

The starting **hydrolyzed tetrodotoxin carboxylate 3** is:



Formation of D. The boxed hydroxyl is attached to C7. Of its neighboring carbons, C6 has no hydrogen, whereas C8 does. Elimination therefore removes the C7 hydroxyl and the C8 hydrogen, giving the C7=C8 enol.

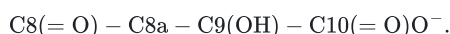
This **initial enol tautomer of D** is:



Keto–enol tautomerization gives the **C8 ketone D** listed in the Answers. To draw it from **3**:

- Replace C7–OH by a methylene group at C7.
- Replace C8–OH and C8–H by a carbonyl at C8.
- Retain the remaining substituents and stereochemistry.

Formation of E and F. In the ketone tautomer of **D**, the relevant sequence is



This is a β-hydroxy carbonyl arrangement. Base removes the C9 hydroxyl proton; the resulting oxygen lone pair forms the C9 carbonyl while the **C8a–C9 bond breaks**. The ring fragment becomes an enolate.

The detached two-carbon fragment is **glyoxylate F**, $\text{O}=\text{CC}(=\text{O})[\text{O}^-]$. Protonation of the ring enolate on oxygen gives the **enol E** listed above.

To draw **E**, remove the entire C9–C10 side chain from **D**, replace the C8 carbonyl by C8–OH, and draw a C8=C8a double bond. Its remaining stereocenters retain their configurations.

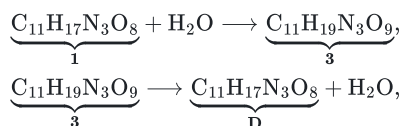
Formation of 2. The product is **2-amino-6-(hydroxymethyl)quinazolin-8-ol**, Nc1ncc2cc(CO)cc(O)c2n1.

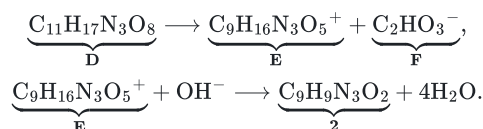
Starting from the enol representation of **E**, the three dehydrations are:

Hydroxyl removed	Hydrogen removed	Double bond formed
C4–OH	N3–H	N3=C4
C5–OH	C4a–H	C4a=C5
C6–OH	C7–H	C6=C7

The existing C8=C8a bond completes the carbon-ring unsaturation. Deprotonation and redistribution of the guanidinium π bonds give the aromatic quinazoline.

For the protonation states shown, the atom- and charge-balanced equations are





Here water is O , and the hydroxide ion is $[\text{OH}^-]$. The last equation includes three dehydration waters and one water from neutralization.

The overall reaction is consequently



7.3 — Carbon atoms originating from L-arginine

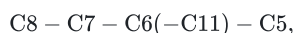
L-Arginine, in the protonation state drawn in the problem, has SMILES:

NC(=[NH2+])NCCC[C@H](N)C(=O)[O-]

Its guanidinium carbon and its uninterrupted five-carbon chain can be mapped onto tetrodotoxin without breaking that chain:

Carbon in L-arginine	Corresponding carbon in tetrodotoxin
Guanidinium carbon	C2
Side-chain carbon adjacent to the guanidino nitrogen, C_δ	C4
C_γ	C4a
C_β	C8a
Amino-acid C_α	C9
Carboxylate carbon	C10

The remaining five-carbon fragment is the branched chain



which matches the prenyl donor's carbon connectivity.

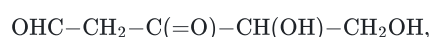
On the original tetrodotoxin drawing, circle:

1. The carbon bonded to all three nitrogens.
2. The hydroxyl-bearing carbon directly bonded to the upper ring NH.
3. Its adjacent methine carbon, C4a.
4. The adjacent quaternary carbon bonded to the other ring NH, C8a.
5. The hydroxyl-bearing methine above that quaternary carbon, C9.
6. The carbon bearing the negatively charged oxygen, C10.

Hydrolysis from **1** to **3** changes oxygen connectivity but preserves these carbon-carbon connections, so the assignment is the same in both drawings.

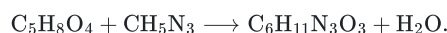
7.4 — Formation and stereochemistry of G

The open-chain **2-deoxy-3-oxo-D-pentose** is



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

Guanidine is N=C(N)N. The molecular formulas require



Only **one water molecule** is lost. Complete condensation at both carbonyl groups would instead lose two waters and give C_6H_9N_3O_2, which is inconsistent with the stated formula.

The cyclic intermediate can form by condensation at the ketone, followed by intramolecular addition of another guanidine nitrogen to the aldehyde. This closes a six-membered ring while retaining the aldehyde oxygen as a hemiaminal hydroxyl. Proton transfers give the enamine tautomer of **G** specified in the Answers.

To draw that tautomer precisely, use the ring sequence



where the C6 substituent is the stereochemically defined dihydroxyethyl group encoded in

NC1=NC([C@H](O)CO)=CC(O)N1.

The original sugar stereocenter retains its spatial configuration. A Fischer projection of the side chain has:

- The heterocyclic ring above the stereocenter.
- The terminal hydroxymethyl group below it.
- The hydroxyl group on the right and hydrogen on the left.

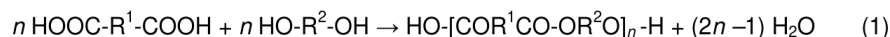
Its descriptor is **S** in **G**, although the corresponding center is **R** in the starting sugar. This change results from a change in CIP priorities when the ketone carbon becomes part of the nitrogen-containing ring; it does **not** represent inversion.

The newly formed hemiaminal carbon has unspecified stereochemistry, consistent with showing its hydroxyl bond as wavy.

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

Problem 8: Polycondensation and the degree of polymerization

The esterification reaction between bi-functional molecules gives one of the typical linear chain polymers, as shown in equation (1), by polycondensation (often called "condensation polymerization"). The control of polymerization conditions and procedures determines the length of polymer strands, i. e. the average degree of polymerization, $\bar{X}$ (note that $\bar{X} = 2n$ in the present instance). Because $\bar{X}$ (and also n) is an averaged number, it is not always an integer but a value with decimal figures.



$\bar{X}$ can be estimated from the consumption of functional groups (here, $-\text{COOH}$ and $-\text{OH}$). Let us define the degree of reaction, p , as $p = (N_0 - N)/N_0$ (≤ 1), where N_0 and N denote the total numbers of functional groups before and after the polymerization, respectively. For each functional group of the dicarboxylic acid molecules (**A**) and diol molecules (**B**), we add the suffixes of "A" or "B" such as N_{A0} , N_{B0} , N_A or N_B , respectively, i. e. $N_0 = N_{A0} + N_{B0}$ and $N = N_A + N_B$. When the initial feed is unbalanced such as $N_{A0} \leq N_{B0}$, $\bar{X}$ is expressed by p_A and r as shown in equation 2, where $r = N_{A0}/N_{B0}$ (≤ 1) and $p_A = (N_{A0} - N_A)/N_{A0}$. If $r = 1$, p_A is identical to p and equation 2 becomes the same to the Carothers equation.

$$\bar{X} = \frac{1+r}{1+r-2p_A r} \quad (2)$$

Some nylon-6,6 sample was prepared by polycondensation between an equimolar mixture of adipic acid (hexanedioic acid) and hexamethylenediamine (hexane-1,6-diamine).

8.1 Show the chemical structure of this nylon-6,6 sample.

[Caution: What are the end groups when polycondensation was started from the equimolar mixture?]

8.2 When an average molar weight, M , of this nylon-6,6 sample is $5507.25 \text{ (g mol}^{-1}\text{)}$, calculate its $\bar{X}$ value to the second decimal place.

8.3 Give the p value to the fifth decimal place that is necessary to prepare the above nylon-6,6 sample. If you get no numerical answer in **8.2** use the value 52.50 instead.

The low-molecular-weight polyester (oligoester) is prepared from the mixture of 36.54 g of adipic acid (hexanedioic acid) and an unknown amount [$W \text{ (g)}$] of butane-1,4-diol (Bdiol). Under the condition of $p_A \rightarrow 1$, the oligoester with $\bar{X} = 11.00$ carrying Bdiol units in both chain ends, is obtained.

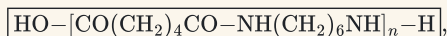
8.4 Show the precise chemical structure of this oligoester of $\bar{X} = 11.00$.

8.5 Calculate the unknown amount, $W \text{ (g)}$, to the first decimal place.

Official English text of the problem.

Answers

- 8.1:** Nylon-6,6, represented by



with carboxyl and amino end groups. Repeat-fragment SMILES: `[ * ]C(=O)CCCC(=O)NCCCCCN[ * ]`; the full-chain construction is specified below.

- 8.2:** $\bar{X} = 48.50$, using the atomic-weight convention stated below.
- 8.3:** $p = 0.97938$.
- 8.4:** Hydroxyl-terminated oligo(butylene adipate), containing **five adipate residues and six butane-1,4-diol residues**. Exact 11-unit-chain SMILES:
`OCCCCOC(=O)CCCC(=O)OCCCCOC(=O)CCCC(=O)OCCCCOC(=O)CCCC(=O)OCCCCOC(=O)CCCC(=O)OCCCCOC(=O)CCCC(=O)OCCCCO`.
- 8.5:** $W = 27.0 \text{ g}$.

Solution

For the numerical calculations, use the two-decimal atomic weights

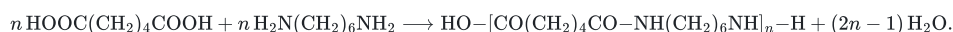
$$A_r(\text{C}) = 12.01, \quad A_r(\text{H}) = 1.01, \quad A_r(\text{N}) = 14.01, \quad A_r(\text{O}) = 16.00.$$

8.1

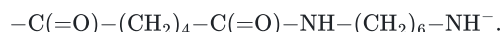
The monomers are:

- Adipic acid (hexanedioic acid)**, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, SMILES `O=C(O)CCCC(=O)O`.
- Hexamethylenediamine (hexane-1,6-diamine)**, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$, SMILES `NCCCCCN`.

A carboxyl group and an amino group condense to form an amide linkage, releasing **water**, H_2O , SMILES o. Connecting n molecules of each monomer into one linear chain requires $2n - 1$ amide bonds. The balanced equation is



Thus, the requested representative **nylon-6,6** chain has one terminal $-\text{COOH}$ group and one terminal $-\text{NH}_2$ group. Its repeating connectivity is



In the repeat-fragment SMILES given above, $[*]$ marks attachment to adjacent units. For any positive integer n , a full-chain SMILES with the displayed end groups is constructed by writing o followed by n consecutive copies of $\text{C}(=\text{O})\text{CCCC}(=\text{O})\text{NCCCCCN}$. A single ordinary molecular SMILES cannot encode a distribution of chain lengths or a noninteger average n .

Strictly, an equimolar feed ensures equal **total** numbers of residual carboxyl and amino groups throughout the sample. It does not require every individual chain to have unlike end groups; the displayed chain represents the balanced composition.

8.2

The monomer and water molar masses are

$$\begin{aligned} M_{\text{adipic acid}} &= 6(12.01) + 10(1.01) + 4(16.00) = 146.16 \text{ g mol}^{-1}, \\ M_{\text{diamine}} &= 6(12.01) + 16(1.01) + 2(14.01) = 116.24 \text{ g mol}^{-1}, \\ M_{\text{water}} &= 2(1.01) + 16.00 = 18.02 \text{ g mol}^{-1}. \end{aligned}$$

Using the balanced condensation equation,

$$\begin{aligned} M &= n(146.16) + n(116.24) - (2n - 1)(18.02) \\ &= 226.36n + 18.02 \quad (\text{g mol}^{-1}). \end{aligned}$$

The 18.02 g mol^{-1} term accounts for the chain ends. Hence,

$$n = \frac{5507.25 - 18.02}{226.36} = 24.25.$$

Because X counts the residues of **both** monomers,

$$X = 2n = 48.50.$$

The noninteger n is an average, as specified in the problem.

8.3

For the equimolar mixture, $r = 1$ and $p_A = p$. Equation (2) gives

$$X = \frac{2}{2 - 2p} = \frac{1}{1 - p}.$$

Therefore,

$$p = 1 - \frac{1}{X} = 1 - \frac{1}{48.50} = 0.979381443 \dots,$$

so, to five decimal places,

$$p = 0.97938.$$

8.4

The diol is **butane-1,4-diol**, $\text{HO}(\text{CH}_2)_4\text{OH}$, SMILES occcco.

In the limit $p_A \rightarrow 1$, all carboxyl groups are esterified. A linear chain ending in diol residues must alternate as



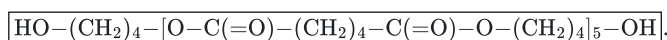
If it contains a acid residues and b diol residues, then

$$b = a + 1, \quad a + b = 11.$$

Consequently,

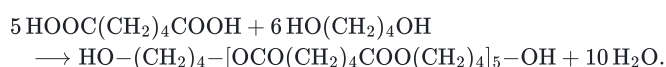
$$a = 5, \quad b = 6.$$

The precise requested 11-unit structure is therefore



This **hydroxyl-terminated oligo(butylene adipate)** has five adipate residues alternating with six diol residues. Both ends are $-\text{CH}_2\text{OH}$, and all ten carboxyl groups have become ester groups. Its full SMILES is given in **Answers 8.4**.

The balanced condensation equation is



The product has molecular formula $\text{C}_{54}\text{H}_{90}\text{O}_{22}$. Since X is an average, the sample may contain different chain lengths; the structure above is the requested 11-unit representative.

8.5

Both monomers are bifunctional, so their initial functional-group ratio equals their molar ratio:

--

$$r = \frac{N_{A0}}{N_{B0}} = \frac{n_{\text{acid}}}{n_{\text{diol}}}.$$

At $p_A \rightarrow 1$,

$$11.00 = \frac{1+r}{1-r},$$

which gives

$$r = \frac{11-1}{11+1} = \frac{5}{6}.$$

The amount of adipic acid is

$$n_{\text{acid}} = \frac{36.54 \text{ g}}{146.16 \text{ g mol}^{-1}} = 0.2500 \text{ mol}.$$

Therefore,

$$n_{\text{diol}} = \frac{6}{5}(0.2500) = 0.3000 \text{ mol}.$$

For butane-1,4-diol,

$$M_{\text{diol}} = 4(12.01) + 10(1.01) + 2(16.00) = 90.14 \text{ g mol}^{-1}.$$

Thus,

$$W = (0.3000 \text{ mol})(90.14 \text{ g mol}^{-1}) = 27.042 \text{ g},$$

and to one decimal place,

$$\boxed{W = 27.0 \text{ g}}.$$

The solution was checked against the official solution.

Problem 9: α-Cyclodextrin

α-Cyclodextrin (αCyD), which is a cyclic oligosaccharide of six α(1→4) linked α-D-glucopyranoside units, can be topologically represented as toroids (Figure 1). α-D-glucopyranoside units in αCyD are usually in the most stable chair conformation.

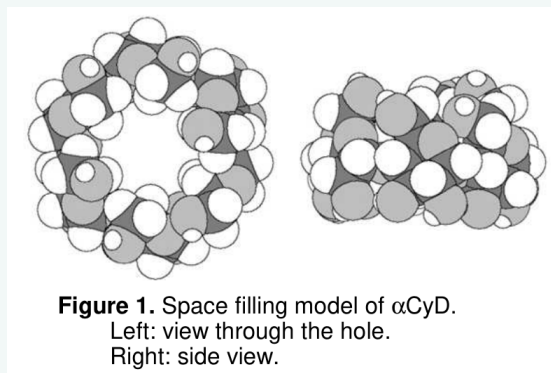
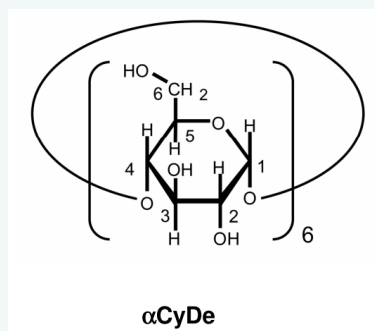


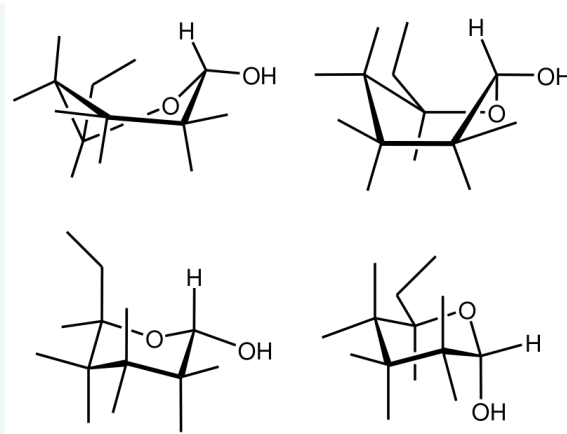
Figure 1. Space filling model of αCyD.

Left: view through the hole.

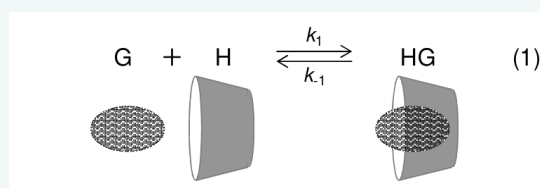
Right: side view.

9.1 Give the absolute configuration (*R* or *S*) at stereogenic carbons C-2 and C-5 of D-glucose. Also, draw a stereostructure of the open chain form of D-glucose.

9.2 Choose the most stable conformation from the following four incomplete α-D-glucopyranose formulas. Also, add four OH groups and four H atoms to complete the α-D-glucopyranose formula.



α CyD in water is able to host hydrophobic molecules. When the host : guest (H : G) stoichiometry is 1 : 1, the inclusion complexation can be given by the following equilibrium.



where k_1 and k_{-1} are the rate constant for the forward and backward reaction, respectively. The complexation of a guest to α CyD causes a chemical shift change in ^1H NMR spectra.

Figure 2 shows a part of ^1H NMR spectra (signals from H-1 of α CyD) showing the chemical shift change in the presence of varying amounts of BTAD (1,10-bis(trimethylammonium)decane diiodide). The doublet peak at 5.06 ppm is from H-1 of free α CyD, while the doublet at 5.14 ppm is from H-1 of α CyD complexed with BTAD. (Note that the spectra given in Figure 2 were measured in the complexation equilibrium state.)

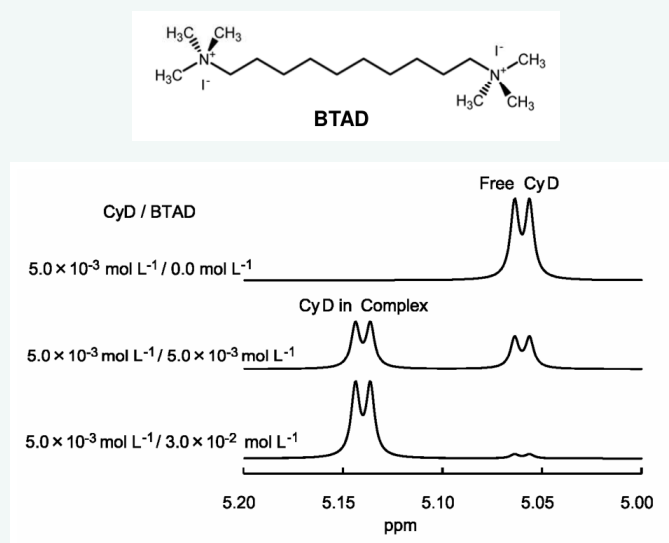


Figure 2.

Expanded ^1H NMR spectra (signals from H-1 of α CyD) of solutions with concentration of α CyD equal to $5.0 \cdot 10^{-3} \text{ mol dm}^{-3}$ and that of BTAD equal from 0 to $3.0 \cdot 10^{-2} \text{ mol dm}^{-3}$.

9.3 Consider a solution in which concentrations of α CyD as well as BTAD are equal to $5.0 \cdot 10^{-3} \text{ mol dm}^{-3}$ and the relative peak areas of the doublets at 5.06 and 5.14 ppm are 0.41 and 0.59, respectively. Calculate (to 2 significant figures) the concentration equilibrium constant, K , for the inclusion complexation of α CyD / BTAD.

Complexation of α CyD with hexyltrimethylammonium bromide (HTAB) appears in NMR spectra in a way different from the α CyD/BTAD complexation. Figure 3 shows a part of ^1H NMR spectra (H-6 signal of HTAB) in α CyD/HTAB solutions. The signal appears as one triplet (not two triplets), which shifts depending on the concentration of α CyD from the position of free HTAB to the position of α CyD/HTAB in proportion to the fraction of the complex in the solution. The H-6 signals from free HTAB and HTAB complexed with α CyD are triplets at 0.740 ppm and 0.860 ppm, respectively.

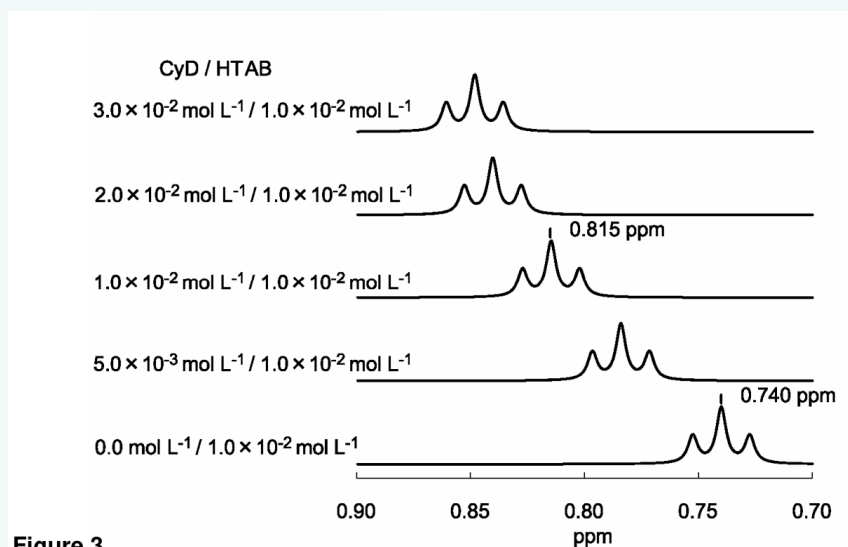
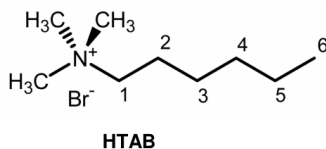


Figure 3.

Figure 3.

Expanded ^1H NMR spectra (H-6 signal of HTAB) of solutions with concentration of HTAB equal to $1.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ and that of αCyD equal from 0 to $3.0 \cdot 10^{-2} \text{ mol dm}^{-3}$.

9.4 The signal of HTAB in αCyD /HTAB solutions appears as one triplet that shifts depending on the concentration of αCyD . Choose the rational interpretation(s) just from these spectra.

Hint: When a guest molecule move in and out of αCyD rapidly and repeatedly, only one signal of the guest is observed at the weighted average of the chemical shifts of the free guest and the shift of the guest included in αCyD .

- a) k_1 of αCyD /HTAB $>$ k_1 of αCyD /BTAD
- b) k_1 of αCyD /HTAB $<$ k_1 of αCyD /BTAD
- c) K of αCyD /HTAB $>$ K of αCyD /BTAD
- d) K of αCyD /HTAB $<$ K of αCyD /BTAD

9.5 The signals of HTAB in the solution with concentrations of αCyD as well as HTAB equal to $1.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ are positioned at 0.815 ppm. Calculate (to 2 significant figures) the value of K for the complexation of αCyD /HTAB.

9.6 At 40.0 °C and 60.0 °C, K for the complexation of αCyD / HTAB are $3.12 \cdot 10^2$ and $2.09 \cdot 10^2$ respectively. Calculate (to 2 significant figures) the enthalpy change, ΔH° [kJ mol^{-1}] and the entropy change, ΔS° [$\text{J K}^{-1} \text{mol}^{-1}$]. (Ignore the temperature dependence of ΔH° and ΔS° .)

Official English text of the problem.

Answers

- **9.1: C-2: *R*; C-5: *R*.** Open-chain D-glucose: $\text{O}=\text{C}[\text{C}@\text{H}](\text{O})[\text{C}@@\text{H}](\text{O})[\text{C}@\text{H}](\text{O})[\text{C}@\text{H}](\text{O})\text{CO}$. Its Fischer projection has CHO at the top, CH_2OH at the bottom, and the OH groups at C-2 through C-5 **right, left, right, right**.
- **9.2:** Choose the **lower-right structure**, the $^4\text{C}_1$ chair of $\alpha\text{-D-glucopyranose}$: $\text{OC}[\text{C}@\text{H}]1\text{O}[\text{C}@\text{H}](\text{O})[\text{C}@\text{H}](\text{O})[\text{C}@@\text{H}](\text{O})[\text{C}@@\text{H}]1\text{O}$. The C-1 OH is axial down; the C-2, C-3 and C-4 OH groups and C-5 CH_2OH group are equatorial. Complete the labels as specified below.
- **9.3:** $K_{\text{BTAD}} = 7.0 \times 10^2 \text{ dm}^3 \text{mol}^{-1}$.
- **9.4: a)** is the intended qualitative interpretation of the exchange pattern. The quantitative population data also establish **d)**; see the qualification below.
- **9.5:** $K_{\text{HTAB}} = 4.4 \times 10^2 \text{ dm}^3 \text{mol}^{-1}$.
- **9.6:** $\Delta H^\circ = -17 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -7.7 \text{ J K}^{-1} \text{mol}^{-1}$.

Solution

9.1

The required Fischer projection of open-chain D-glucose has the carbon chain vertical, with the aldehyde group CHO uppermost and CH₂OH at the bottom.

Stereogenic carbon	Left-hand substituent	Right-hand substituent
C-2	H	OH
C-3	OH	H
C-4	H	OH
C-5	H	OH

In a Fischer projection, horizontal bonds point towards the viewer and vertical bonds point away.

At **C-2**, the CIP priorities are

$$\text{OH} > \text{C-1 side} > \text{C-3 side} > \text{H}.$$

The aldehyde carbon is compared as attached to (O, O, H), whereas C-3 is attached to (O, C, H). Therefore the aldehyde side has higher priority. Accounting for the horizontal hydrogen pointing towards the viewer gives *R*.

At **C-5**, the priorities are

$$\text{OH} > \text{C-4 side} > \text{CH}_2\text{OH} > \text{H}.$$

The C-4 side has attached atoms (O, C, H), whereas C-6 has (O, H, H). The same Fischer-projection analysis gives *R*.

Thus

$$\boxed{\text{C-2: } R, \quad \text{C-5: } R}.$$

The complete open-chain configuration is (2*R*, 3*S*, 4*R*, 5*R*).

9.2

The **lower-right drawing** is the stable ⁴C₁ chair. Complete it according to this table; "up" and "down" refer to the two faces of the ring.

Carbon	Oxygen-containing substituent	Hydrogen
C-1	OH: axial, down	Equatorial, up
C-2	OH: equatorial, down	Axial, up
C-3	OH: equatorial, up	Axial, down
C-4	OH: equatorial, down	Axial, up
C-5	CH ₂ OH: equatorial, up	Axial, down

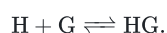
Specifically, add the four missing OH labels at **C-2, C-3, C-4, and the end of the C-6 side chain**. Add the four missing H labels at **C-2, C-3, C-4, and C-5**.

This chair places the three non-anomeric ring hydroxyl groups and the hydroxymethyl group equatorial, minimizing unfavorable axial interactions. For the α anomer, the anomeric hydroxyl group is on the opposite face from the C-5 hydroxymethyl group, so it is axial down in this chair.

The SMILES given above specifies the stereoisomer; the chair conformation and axial/equatorial placements are specified by the table.

9.3

Let H denote the host, G the guest, and HG their 1:1 inclusion complex:



The concentration equilibrium constant is

$$K = \frac{[\text{HG}]}{[\text{H}][\text{G}]}.$$

Each free or complexed host contributes the same number of H-1 protons. Consequently, the integrated peak areas give the fractions of host in the two states:

$$f_{\text{free}} = 0.41, \quad f_{\text{complexed}} = 0.59.$$

With total host and guest concentrations both equal to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$,

$$\begin{aligned} [\text{HG}] &= 0.59(5.0 \times 10^{-3}) = 2.95 \times 10^{-3} \text{ mol dm}^{-3}, \\ [\text{H}] &= 0.41(5.0 \times 10^{-3}) = 2.05 \times 10^{-3} \text{ mol dm}^{-3}. \end{aligned}$$

The 1:1 stoichiometry and equal total concentrations give

$$[\text{G}] = 5.0 \times 10^{-3} - 2.95 \times 10^{-3} = 2.05 \times 10^{-3} \text{ mol dm}^{-3}.$$

Therefore,

$$K_{\text{BTAD}} = \frac{2.95 \times 10^{-3}}{(2.05 \times 10^{-3})^2} = 701.96 \text{ dm}^3 \text{ mol}^{-1},$$

or, to two significant figures,

$$K_{\text{BTAD}} = 7.0 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}.$$

9.4

For HTAB, the single triplet at an intermediate chemical shift indicates **rapid exchange between free and bound states on the NMR timescale**. Its observed shift is

$$\delta_{\text{obs}} = (1 - f)\delta_{\text{free}} + f\delta_{\text{bound}},$$

where f is the fraction of guest bound.

For BTAD, separate free-host and complexed-host doublets remain visible, indicating **slow exchange on the NMR timescale**.

The intended qualitative kinetic interpretation is therefore **a)**: faster association/exchange for HTAB.

An averaged signal does not itself establish stronger or weaker equilibrium binding. At equilibrium,

$$k_1[\text{H}][\text{G}] = k_{-1}[\text{HG}], \quad K = \frac{k_1}{k_{-1}}.$$

Both forward and reverse exchange can become faster without increasing their ratio. Thus **neither c) nor d) follows merely from the distinction between averaged and separate signals**.

Using the quantitative populations, however, parts 9.3 and 9.5 establish

$$K_{\text{HTAB}} < K_{\text{BTAD}},$$

so **d) is also supported when the numerical information in the spectra is included**.

9.5

Let f be the fraction of HTAB present in the complex. The weighted-average shift gives

$$0.815 = (1 - f)(0.740) + f(0.860).$$

Hence

$$f = \frac{0.815 - 0.740}{0.860 - 0.740} = \frac{0.075}{0.120} = 0.625.$$

The total guest concentration is $1.0 \times 10^{-2} \text{ mol dm}^{-3}$, so

$$[\text{HG}] = 0.625(1.0 \times 10^{-2}) = 6.25 \times 10^{-3} \text{ mol dm}^{-3}.$$

Because the total host and guest concentrations are equal,

$$[\text{H}] = [\text{G}] = 1.0 \times 10^{-2} - 6.25 \times 10^{-3} = 3.75 \times 10^{-3} \text{ mol dm}^{-3}.$$

Therefore,

$$K_{\text{HTAB}} = \frac{6.25 \times 10^{-3}}{(3.75 \times 10^{-3})^2} = 444.44 \text{ dm}^3 \text{ mol}^{-1},$$

giving

$$K_{\text{HTAB}} = 4.4 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}.$$

9.6

Convert the temperatures to kelvin:

$$T_1 = 313.15 \text{ K}, \quad T_2 = 333.15 \text{ K}.$$

For thermodynamic logarithms, use the dimensionless constant $K^\circ = Kc^\circ$, with $c^\circ = 1 \text{ mol dm}^{-3}$. Its numerical values are therefore 312 and 209.

Assuming temperature-independent ΔH° , the integrated van 't Hoff equation is

$$\ln \left(\frac{K_2^\circ}{K_1^\circ} \right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

Using $R = 8.31446 \text{ J K}^{-1} \text{ mol}^{-1}$,

$$\Delta H^\circ = -\frac{R \ln(209/312)}{1/333.15 - 1/313.15} = -1.73773 \times 10^4 \text{ J mol}^{-1}.$$

Thus

$$\Delta H^\circ = -17 \text{ kJ mol}^{-1}.$$

The negative sign agrees with the decrease of K as temperature increases.

Next,

$$\Delta G^\circ = -RT \ln K^\circ = \Delta H^\circ - T\Delta S^\circ,$$

so

$$\Delta S^\circ = R \ln K^\circ + \frac{\Delta H^\circ}{T}.$$

Using T_1 and retaining the unrounded enthalpy,

$$\Delta S^\circ = (8.31446) \ln 312 + \frac{-17377.3}{313.15} = -7.7419 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Therefore,

$$\boxed{\Delta S^\circ = -7.7 \text{ J K}^{-1} \text{ mol}^{-1}}.$$

The solution was checked against the official solution.