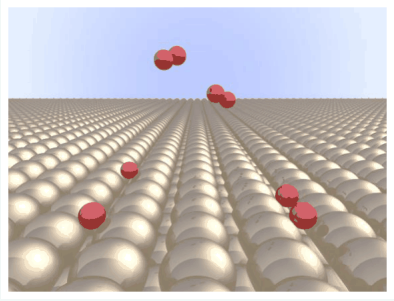
IChO 2021

Theory problems and solutions · Osaka, Japan (held remotely) · 9 theory problems with complete solutions

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Problem 1: Hydrogen at a Metal Surface



Hydrogen is expected to be a future energy source that does not depend on fossil fuels. Here, we will consider the hydrogen-storage process in a metal, which is related to hydrogen-transport and -storage technology.

PART A

As hydrogen is absorbed into the bulk of a metal via its surface, let us first consider the adsorption process of hydrogen at the metal surface, $\mathrm{H_2\,(g)} \longrightarrow 2\,\mathrm{H\,(ad)}$, where the gaseous and adsorbed states of hydrogen are represented as (g) and (ad), respectively. Hydrogen molecules ($\mathrm{H_2}$) that reach the metal surface (M) dissociate at the surface and are adsorbed as H atoms (Fig. 1). Here, the potential energy of $\mathrm{H_2}$ is represented by two variables: the interatomic distance, d, and the height relative to the surface metal atom, z. It is assumed that the axis along the two H atoms is parallel to the surface and that the center of gravity is always on the vertical dotted line in Fig. 1. Fig. 2 shows the potential energy contour plot for the dissociation at the surface. The numerical values represent the potential energy in units of kJ per mole of $\mathrm{H_2}$. The solid line spacing is $20\ \mathrm{kJ\,mol^{-1}}$, the dashed line spacing is $100\ \mathrm{kJ\,mol^{-1}}$, and the spacing between solid and dashed lines is $80\ \mathrm{kJ\,mol^{-1}}$. The zero-point vibration energy is ignored.

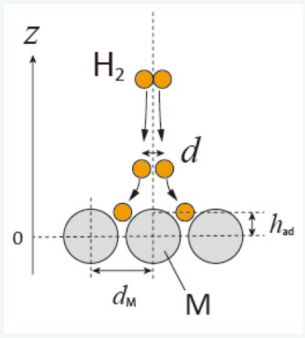


Fig.1 Definition of variables. Drawing is not in scale.

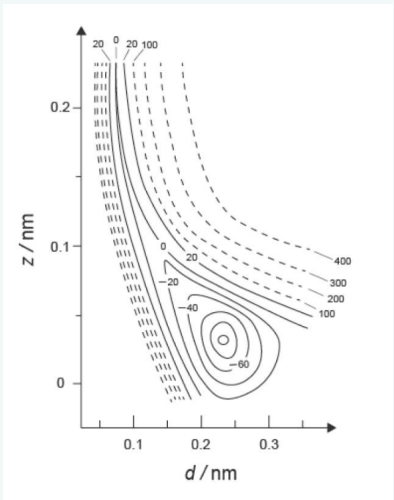


Fig.2

1.1 For each of the following items (i)–(iii), select the closest value from A–G.

(i) The interatomic distance for a gaseous $\mathrm{H_2}$ molecule

(ii) The interatomic distance between metal atoms (d_{M} in Fig. 1)

(iii) The distance of adsorbed H atoms from the surface (h_{AD} in Fig. 1)

A. $0.03\ \mathrm{nm}$	**B.** $0.07\ \mathrm{nm}$	**C.** $0.11\ \mathrm{nm}$	**D.** $0.15\ \mathrm{nm}$
E. $0.19\ \mathrm{nm}$	F. $0.23\ \mathrm{nm}$	G. $0.27\ \mathrm{nm}$	

1.2 For each of the following items (i)–(ii), select the closest value from A–H.

(i) the energy required for the dissociation of gaseous $\mathrm{H_2}$ to gaseous H [$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(g)}$]

(ii) the energy released during the adsorption of a gaseous $\mathrm{H_2}$ [$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(ad)}$]

A. $20\ \mathrm{kJ\,mol^{-1}}$	**B.** $40\ \mathrm{kJ\,mol^{-1}}$	**C.** $60\ \mathrm{kJ\,mol^{-1}}$	**D.** $100\ \mathrm{kJ\,mol^{-1}}$
E. $150\ \mathrm{kJ\,mol^{-1}}$	F. $200\ \mathrm{kJ\,mol^{-1}}$	G. $300\ \mathrm{kJ\,mol^{-1}}$	H. $400\ \mathrm{kJ\,mol^{-1}}$

PART B

The adsorbed hydrogen atoms are then either absorbed into the bulk, or recombine and desorb back into the gas phase, as shown in the reactions (1a) and (1b). $\mathrm{H\,(ab)}$ represents a hydrogen atom absorbed in the bulk.

$$\mathrm{H_2(g)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{2H(ad)} \tag{1a}$$

$$\mathrm{H(ad)} \xrightarrow{k_3} \mathrm{H(ab)} \tag{1b}$$

The reaction rates per surface site for adsorption, desorption, and absorption are $r_1[\mathrm{s^{-1}}]$, $r_2[\mathrm{s^{-1}}]$ and $r_3[\mathrm{s^{-1}}]$, respectively. They are expressed as:

$$r_1 = k_1 P_{\mathrm{H_2}} (1-\theta)^2 \tag{2}$$

$$r_2 = k_2 \theta^2 \tag{3}$$

$$r_3 = k_3 \theta \tag{4}$$

where $k_1\ [\mathrm{s^{-1}\,Pa^{-1}}]$, $k_2\ [\mathrm{s^{-1}}]$ and $k_3\ [\mathrm{s^{-1}}]$ are the reaction rate constants and $P_{\mathrm{H_2}}$ is the pressure of $\mathrm{H_2}$. Among the sites available on the surface, θ ($0 \leq \theta \leq 1$) is the fraction occupied by H atoms. It is assumed that adsorption and desorption are fast compared to absorption ($r_1, r_2 \gg r_3$) and that θ remains constant.

1.3 r_3 can be expressed as:

$$r_3 = \frac{k_3}{1 + \sqrt{\dfrac{1}{P_{\mathrm{H_2}} C}}} \tag{5}$$

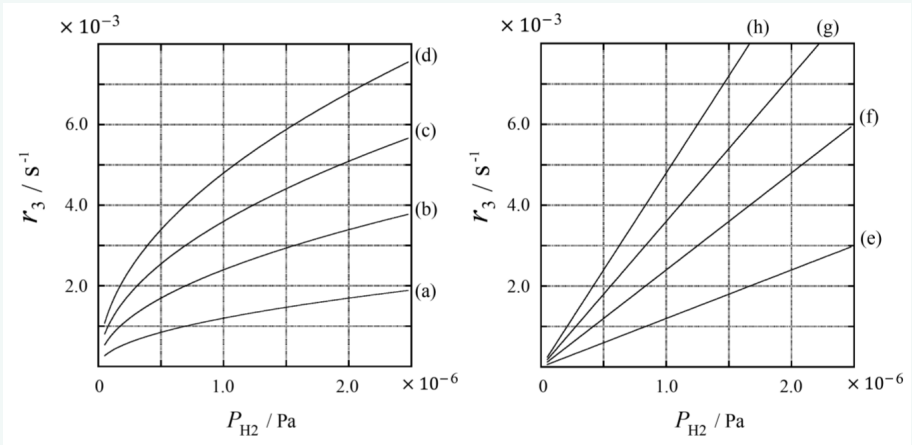
Express C using k_1 and k_2.

A metal sample with a surface area of $S = 1.0 \times 10^{-3}\ \mathrm{m^2}$ was placed in a container ($1\mathrm{L} = 1.0 \times 10^{-3}\ \mathrm{m^3}$) with $\mathrm{H_2}$ ($P_{\mathrm{H_2}} = 1.0 \times 10^{2}\ \mathrm{Pa}$). The density of hydrogen-atom adsorption sites on the surface was $N = 1.3 \times 10^{18}\ \mathrm{m^{-2}}$. The surface temperature was kept at $T = 400\ \mathrm{K}$. As the reaction (1) proceeded, $P_{\mathrm{H_2}}$ decreased at a constant rate of $v = 4.0 \times 10^{-4}\ \mathrm{Pa\,s^{-1}}$. Assume that $\mathrm{H_2}$ is an ideal gas and that the volume of the metal sample is negligible.

1.4 Calculate the amount of H atoms in moles absorbed per unit area of the surface per unit time, $A\ [\mathrm{mol\,s^{-1}\,m^{-2}}]$.

1.5 At $T = 400\ \mathrm{K}$, C equals $1.0 \times 10^{2}\ \mathrm{Pa^{-1}}$. Calculate the value of k_3 at $400\ \mathrm{K}$. If you did not obtain the answer to **1.4**, use $A = 3.6 \times 10^{-7}\ \mathrm{mol\,s^{-1}\,m^{-2}}$.

1.6 At a different T, $C = 2.5 \times 10^{3}\ \mathrm{Pa^{-1}}$ and $k_3 = 4.8 \times 10^{-2}\ \mathrm{s^{-1}}$ are given. For r_3 as a function of $P_{\mathrm{H_2}}$ at this temperature, select the correct plot from (a)–(h).



Official English text of the problem.

Answers

- **1.1(i): B —** $0.07\ \mathrm{nm}$.
- **1.1(ii): F —** $0.23\ \mathrm{nm}$.
- **1.1(iii): A —** $0.03\ \mathrm{nm}$.
- **1.2(i): H —** $400\ \mathrm{kJ\,mol^{-1}}$ required.
- **1.2(ii): D —** $100\ \mathrm{kJ\,mol^{-1}}$ released.
- **1.3:** $C = \dfrac{k_1}{k_2}$.
- **1.4:** $A = 2.4 \times 10^{-7}\ \mathrm{mol\,s^{-1}\,m^{-2}}$.
- **1.5:** $k_3 = 1.1 \times 10^{-1}\ \mathrm{s^{-1}}$.
- **1.6: Plot (b).**

Solution

Hydrogen gas is dihydrogen, $\mathrm{H_2}$, SMILES `[H][H]`. Atomic hydrogen, H, has SMILES `[H]`. The labels (ad) and (ab) specify hydrogen at the surface and within the bulk, respectively; SMILES does not encode these environments or the metal–hydrogen coordination.

1.1

(i) Far from the surface, at large z, the minimum-energy molecular configuration occurs at approximately

$$d = 0.07\ \mathrm{nm}.$$

This is the equilibrium bond length of gaseous dihydrogen. The answer is **B**.

(ii) The minimum corresponding to the adsorbed state is located at approximately

$$(d, z) = (0.23,\ 0.03)\ \mathrm{nm}.$$

In Fig. 1, the two adsorbed hydrogen atoms occupy equivalent positions on opposite sides of the central metal atom. Their horizontal coordinates relative to that atom are $-d_{\mathrm{M}}/2$ and $+d_{\mathrm{M}}/2$, so their separation equals d_{M}. Thus,

$$d_{\mathrm{M}} = d_{\mathrm{adsorbed}} \quad \approx 0.23\ \mathrm{nm},$$

giving **F**.

(iii) The vertical coordinate of the same minimum gives the adsorption height:

$$h_{\mathrm{AD}} = z_{\mathrm{min}} \approx 0.03\ \mathrm{nm}.$$

The answer is **A**.

1.2

The energy reference is the minimum for the gaseous molecule, approximately $0\ \mathrm{kJ\,mol^{-1}}$. All energies in Fig. 2 are per mole of $\mathrm{H_2}$.

(i) For dissociation,

$$\mathrm{H_2\,(g)} \longrightarrow 2\,\mathrm{H\,(g)},$$

both atoms must be far from the surface and far from each other: large z and large d. The high-energy contours indicate a dissociation energy closest to

$$\boxed{400\ \mathrm{kJ\,mol^{-1}}}.$$

The answer is **H**.

(ii) For dissociative adsorption,

$$\mathrm{H_2\,(g)} \longrightarrow 2\,\mathrm{H\,(ad)},$$

the final state is the minimum near $(0.23, 0.03)\ \mathrm{nm}$. Following the solid contours in $20\ \mathrm{kJ\,mol^{-1}}$ increments places this minimum at approximately $-100\ \mathrm{kJ\,mol^{-1}}$. Consequently,

$$\Delta E_{\mathrm{ads}} \ \approx -100\ \mathrm{kJ\,mol^{-1}},$$

and the positive amount of energy released is

$$\boxed{100\ \mathrm{kJ\,mol^{-1}}}.$$

The answer is **D**.

1.3

The reactions are

$$\mathrm{H_2\,(g)} \rightleftharpoons 2\,\mathrm{H\,(ad)}$$

and

$$\mathrm{H\,(ad)} \longrightarrow \mathrm{H\,(ab)}.$$

Each adsorption event creates two adsorbed atoms, each desorption event removes two, and each absorption event removes one. Constant coverage therefore requires

$$\frac{d\theta}{dt} = 2r_1 - 2r_2 - r_3 = 0.$$

Because $r_1, r_2 \gg r_3$, adsorption and desorption are in approximate equilibrium:

$$k_1 P_{\mathrm{H_2}} (1-\theta)^2 \simeq k_2 \theta^2.$$

Taking the nonnegative square root gives

$$\frac{\theta}{1-\theta} = \sqrt{\frac{k_1 P_{\mathrm{H_2}}}{k_2}}.$$

Within this approximation,

$$\theta = \frac{1}{1 + \sqrt{\dfrac{k_2}{k_1 P_{\mathrm{H_2}}}}},$$

so

$$r_3 = k_3\theta = \frac{k_3}{1 + \sqrt{\dfrac{k_2}{k_1 P_{\mathrm{H_2}}}}}.$$

Comparison with equation (5) yields

$$\boxed{C = \frac{k_1}{k_2}}.$$

Its units are $\mathrm{Pa^{-1}}$, making $P_{\mathrm{H_2}}C$ dimensionless.

1.4

Use the ideal-gas equation with $R = 8.314\ \mathrm{Pa\,m^3\,mol^{-1}\,K^{-1}}$:

$$n_{\mathrm{H_2}} = \frac{P_{\mathrm{H_2}} V}{RT}.$$

At constant volume and temperature, the rate of disappearance of gaseous dihydrogen is

$$-\frac{dn_{\mathrm{H_2}}}{dt} = \frac{Vv}{RT} = \frac{(1.0\times10^{-3}\ \mathrm{m^3})(4.0\times10^{-4}\ \mathrm{Pa\,s^{-1}})}{(8.314\ \mathrm{Pa\,m^3\,mol^{-1}\,K^{-1}})(400\ \mathrm{K})} = 1.20\times10^{-10}\ \mathrm{mol\,s^{-1}}.$$

Since the surface coverage remains constant, hydrogen does not accumulate on the surface. The net process is therefore

$$\mathrm{H_2\,(g)} \longrightarrow 2\,\mathrm{H\,(ab)}.$$

Two moles of hydrogen atoms enter the bulk for each mole of gas consumed. Dividing by the surface area,

$$A = \frac{2Vv}{RTS} = \frac{2(1.20\times10^{-10}\ \mathrm{mol\,s^{-1}})}{1.0\times10^{-3}\ \mathrm{m^2}}.$$

Thus,

$$\boxed{A = 2.4\times10^{-7}\ \mathrm{mol\,s^{-1}\,m^{-2}}}.$$

1.5

At the stated pressure,

$$P_{\mathrm{H_2}}C = (1.0\times10^{2}\ \mathrm{Pa})(1.0\times10^{2}\ \mathrm{Pa^{-1}}) = 1.0\times10^{4}.$$

Hence,

$$\theta = \frac{1}{1 + (P_{\mathrm{H_2}}C)^{-1/2}} = \frac{1}{1+0.010} = 0.9901.$$

Each absorption event transfers one hydrogen atom. Using $N_{\mathrm{A}} = 6.022\times10^{23}\ \mathrm{mol^{-1}}$, the molar absorption rate and the rate per surface site satisfy

$$A = \frac{N r_3}{N_{\mathrm{A}}} = \frac{N k_3 \theta}{N_{\mathrm{A}}}.$$

Therefore, using the unrounded result from **1.4**,

$$k_3 = \frac{A N_{\mathrm{A}}}{N\theta} = \frac{(2.405\times10^{-7}\ \mathrm{mol\,s^{-1}\,m^{-2}})(6.022\times10^{23}\ \mathrm{mol^{-1}})}{(1.3\times10^{18}\ \mathrm{m^{-2}})(0.9901)} = 0.1125\ \mathrm{s^{-1}}.$$

To two significant figures,

$$\boxed{k_3 = 1.1\times10^{-1}\ \mathrm{s^{-1}}}.$$

1.6

Rewrite equation (5) as

$$r_3 = k_3 \frac{\sqrt{C P_{\mathrm{H_2}}}}{1 + \sqrt{C P_{\mathrm{H_2}}}}.$$

Over the plotted pressure range,

$$C P_{\mathrm{H_2}} \le (2.5\times10^{3}\ \mathrm{Pa^{-1}})(2.5\times10^{-6}\ \mathrm{Pa}) = 6.25\times10^{-3} \ll 1.$$

Thus, approximately,

$$r_3 \simeq k_3 \sqrt{C P_{\mathrm{H_2}}}.$$

The curve starts at the origin, rises with increasing pressure, and bends downward. This selects the family (a)–(d).

To identify its magnitude, take $P_{\mathrm{H_2}} = 1.0 \times 10^{-6}\ \mathrm{Pa}$. Then

$$\sqrt{CP_{\mathrm{H_2}}} = \sqrt{(2.5 \times 10^{3})(1.0 \times 10^{-6})} = 0.050,$$

and the full expression gives

$$r_3 = (4.8 \times 10^{-2})\frac{0.050}{1.050} = 2.29 \times 10^{-3}\ \mathrm{s^{-1}}.$$

The low-pressure approximation gives $2.4 \times 10^{-3}\ \mathrm{s^{-1}}$, matching the scale of **curve (b)**. Thus,

$$\boxed{\text{Plot (b)}}.$$

The solution was checked against the official solution.

Problem 2: Isotope Time Capsule



Molecular entities that differ only in isotopic composition, such as $\mathrm{CH_4}$ and $\mathrm{CH_3D}$, are called isotopologues. Isotopologues are considered to have the same chemical characteristics. In nature, however, there exists a slight difference.

Assume that all of the substances shown in this Question are in a gas phase.

Let us consider the following equilibrium:

$$^{12}\mathrm{C}^{16}\mathrm{O}_2 + {}^{12}\mathrm{C}^{18}\mathrm{O}_2 \rightleftharpoons 2\,{}^{12}\mathrm{C}^{16}\mathrm{O}^{18}\mathrm{O} \qquad K = \frac{[{}^{12}\mathrm{C}^{16}\mathrm{O}^{18}\mathrm{O}]^2}{[{}^{12}\mathrm{C}^{16}\mathrm{O}_2][{}^{12}\mathrm{C}^{18}\mathrm{O}_2]} \tag{1}$$

The entropy, S, increases with increasing the number of possible microscopic states of a system, W:

$$S = k_{\mathrm{B}} \ln W \tag{2}$$

$W = 1$ for $^{12}\mathrm{C}\,^{16}\mathrm{O}_2$ and $^{12}\mathrm{C}\,^{18}\mathrm{O}_2$. In contrast, $W = 2$ for a $^{12}\mathrm{C}\,^{16}\mathrm{O}\,^{18}\mathrm{O}$ molecule because the oxygen atoms are distinguishable in this molecule. As the right-hand side of the equilibrium shown in eq. 1 has two $^{12}\mathrm{C}\,^{16}\mathrm{O}\,^{18}\mathrm{O}$ molecules, $W = 2^2 = 4$.

2.1 The enthalpy change, ΔH, of eq. 3 is positive regardless of the temperature.

$$\mathrm{H_2} + \mathrm{DI} \rightleftharpoons \mathrm{HD} + \mathrm{HI} \tag{3}$$

Calculate the equilibrium constants, K, for eq. 3 at very low (think of $T \to 0$) and very high (think of $T \to +\infty$) temperatures. Assume that the reaction remains unchanged at these temperatures and that ΔH converges to a constant value for high temperatures.

The ΔH of the following process can be explained by molecular vibrations.

$$2\mathrm{HD} \rightleftharpoons \mathrm{H_2} + \mathrm{D_2} \qquad K = \frac{[\mathrm{H_2}][\mathrm{D_2}]}{[\mathrm{HD}]^2} \tag{4}$$

At $T = 0\ \mathrm{K}$, the vibrational energy of a diatomic molecule whose vibration frequency is $\nu\ [\mathrm{s^{-1}}]$ is expressed as:

$$E = \frac{1}{2}h\nu \tag{5}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{6}$$

Wherein k is the force constant and μ the reduced mass, which is expressed in terms of the mass of the two atoms in the diatomic molecule, m_1 and m_2, according to:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7}$$

2.2 The vibration of $\mathrm{H_2}$ is at $4161.0\ \mathrm{cm^{-1}}$ when reported as a wavenumber.

Calculate the ΔH of the following equation at $T = 0\ \mathrm{K}$ in units of $\mathrm{J\,mol^{-1}}$.

$$2\mathrm{HD} \rightarrow \mathrm{H_2} + \mathrm{D_2} \tag{8}$$

Assume that:

- only the vibrational energy contributes to the ΔH.
- the k values for $\mathrm{H_2}$, HD, and $\mathrm{D_2}$ are identical.
- the mass of H to be $1\ \mathrm{Da}$ and the mass of D to be $2\ \mathrm{Da}$.

The molar ratio of $\mathrm{H_2}$, HD, and $\mathrm{D_2}$ depends on the temperature in a system in equilibrium. Here, $\Delta_{\mathrm{D_2}}$ is defined as the change of the molar ratio of $\mathrm{D_2}$.

$$\Delta_{\mathrm{D_2}} = \frac{R_{\mathrm{D_2}}}{R^*_{\mathrm{D_2}}} - 1 \tag{9}$$

Here, $R_{\mathrm{D_2}}$ refers to $\dfrac{[\mathrm{D_2}]}{[\mathrm{H_2}]}$ in the sample and $R^*_{\mathrm{D_2}}$ to $\dfrac{[\mathrm{D_2}]}{[\mathrm{H_2}]}$ at $T \rightarrow +\infty$. It should be noted here that the distribution of isotopes becomes random at $T \rightarrow +\infty$.

2.3 Calculate $\Delta_{\mathrm{D_2}}$ with natural D abundance when the isotopic exchange is in equilibrium at the temperature where K in eq. 4 is 0.300. Assume that the natural abundance ratios of D and H are 1.5576×10^{-4} and $1 - 1.5576 \times 10^{-4}$, respectively.

In general, the molar ratio of the doubly substituted isotopologue, which contains two heavy isotope atoms in one molecule, increases with decreasing temperature. Let us consider the molar ratio of $\mathrm{CO_2}$ molecules with molecular weights of 44 and 47, which are described as $\mathrm{CO_2}[44]$ and $\mathrm{CO_2}[47]$ below. The quantity Δ_{47} is defined as:

$$\Delta_{47} = \frac{R_{47}}{R^*_{47}} - 1 \tag{10}$$

R_{47} refers to $\dfrac{[\mathrm{CO_2}[47]]}{[\mathrm{CO_2}[44]]}$ in the sample and R^*_{47} to $\dfrac{[\mathrm{CO_2}[47]]}{[\mathrm{CO_2}[44]]}$ at $T \rightarrow +\infty$. The natural abundances of carbon and oxygen atoms are shown below; ignore isotopes that are not shown here.

	$^{12}\mathrm{C}$	$^{13}\mathrm{O}$
natural abundance	0.988888	0.011112

	$^{16}\mathrm{O}$	$^{17}\mathrm{O}$	$^{18}\mathrm{O}$
natural abundance	0.997621	0.0003790	0.0020000

The temperature dependence of Δ_{47} is determined as follows, where T is given as the absolute temperature in units of K:

$$\Delta_{47} = \frac{36.2}{T^2} + 2.920 \times 10^{-4} \tag{11}$$

2.4 The Δ_{47} of fossil plankton obtained from the Antarctic seabed was 4.50865×10^{-5}.

Estimate the temperature using this R_{47}. This temperature is interpreted as the air temperature during the era in which the plankton lived. Consider only the most common isotopologue of $\mathrm{CO_2}[47]$ for the calculation.

Official English text of the problem.

Answers

- **2.1:** $\lim_{T \to 0} K = 0, \qquad \lim_{T \to +\infty} K = 2.$
- **2.2:** $\Delta H(0) = -6.208 \times 10^2\ \mathrm{J\,mol^{-1}}$, per mole of reaction as written.
- **2.3:** $\Delta_{\mathrm{D_2}} = 0.199925\ldots \approx 0.200$, corresponding to a 20.0% increase in the ratio relative to its random-distribution value.
- **2.4:** With the intended reading $R_{47} = 4.50865 \times 10^{-5}$, $T \approx 295.3\ \mathrm{K} \approx 22.2\ ^\circ\mathrm{C}$. If the number is read literally as Δ_{47}, there is **no real temperature** satisfying eq. 11.

Solution

2.1

The balanced isotope-exchange reaction is

$$\mathrm{H_2} + \mathrm{DI} \rightleftharpoons \mathrm{HD} + \mathrm{HI}, \qquad K = \frac{[\mathrm{HD}][\mathrm{HI}]}{[\mathrm{H_2}][\mathrm{DI}]}.$$

The species are dihydrogen $\mathrm{H_2}$, `[1H][1H]`; deuterium iodide DI, `[2H]I`; hydrogen deuteride HD, `[1H][2H]`; and hydrogen iodide HI, `[1H]I`.

The thermodynamic relation is

$$\ln K = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}.$$

At very low temperature, the positive reaction enthalpy makes the products energetically unfavorable. The enthalpy term dominates, so

$$\boxed{\lim_{T \to 0} K = 0}.$$

At very high temperature, the stipulated finite limiting enthalpy gives $\Delta H^\circ/(RT) \rightarrow 0$, and the isotope distribution becomes random.

Let r denote the atomic D/H ratio. Random substitution gives

$$\frac{[\mathrm{HD}]}{[\mathrm{H_2}]} = 2r, \qquad \frac{[\mathrm{DI}]}{[\mathrm{HI}]} = r.$$

The factor of two in the first ratio arises because either of the two hydrogen positions can contain deuterium. Therefore,

$$\boxed{\lim_{T\to+\infty} K = \frac{2r}{r} = 2}.$$

This statistical factor corresponds to an entropy contribution $R\ln 2$.

2.2

The balanced reaction is

$$2\,\mathrm{HD} \longrightarrow \mathrm{H_2} + \mathrm{D_2}.$$

Deuterium gas, $\mathrm{D_2}$, has SMILES `[2H][2H]`.

Using the prescribed atomic masses,

$$\mu_{\mathrm{H_2}} = \frac{1\times 1}{1+1} = \frac{1}{2}\ \mathrm{Da},$$
$$\mu_{\mathrm{HD}} = \frac{1\times 2}{1+2} = \frac{2}{3}\ \mathrm{Da}, \qquad \mu_{\mathrm{D_2}} = \frac{2\times 2}{2+2} = 1\ \mathrm{Da}.$$

Since the force constants are identical, both frequency and wavenumber are proportional to $\mu^{-1/2}$. Consequently,

$$\widetilde{\nu}_{\mathrm{HD}} = 4161.0\sqrt{\frac{1/2}{2/3}} = 4161.0\frac{\sqrt{3}}{2} = 3603.53\ \mathrm{cm^{-1}},$$

$$\widetilde{\nu}_{\mathrm{D_2}} = 4161.0\sqrt{\frac{1/2}{1}} = \frac{4161.0}{\sqrt{2}} = 2942.27\ \mathrm{cm^{-1}}.$$

At $0\ \mathrm{K}$, each molecule contributes its zero-point vibrational energy, $E = \tfrac{1}{2}hc\widetilde{\nu}$. Thus,

$$\begin{aligned}\Delta H(0) &= \frac{N_\mathrm{A}hc}{2}(\widetilde{\nu}_{\mathrm{H_2}} + \widetilde{\nu}_{\mathrm{D_2}} - 2\widetilde{\nu}_{\mathrm{HD}}) \\ &= \frac{N_\mathrm{A}hc}{2}(4.1610\times 10^{5}\ \mathrm{m^{-1}})\left(1 + \frac{1}{\sqrt{2}} - \sqrt{3}\right).\end{aligned}$$

Using the standard constants

$$h = 6.62607015\times 10^{-34}\ \mathrm{J\,s}, \qquad c = 2.99792458\times 10^{8}\ \mathrm{m\,s^{-1}},$$
$$N_\mathrm{A} = 6.02214076\times 10^{23}\ \mathrm{mol^{-1}},$$

gives

$$\boxed{\Delta H(0) = -620.8\ \mathrm{J\,mol^{-1}}}.$$

This is per mole of reaction as written, consuming $2\ \mathrm{mol}$ of HD. The products have the lower total zero-point energy.

2.3

For

$$2\,\mathrm{HD} \rightleftharpoons \mathrm{H_2} + \mathrm{D_2}, \qquad K = \frac{[\mathrm{H_2}][\mathrm{D_2}]}{[\mathrm{HD}]^2} = 0.300,$$

write the atomic fractions as

$$p = 1.5576\times 10^{-4}\quad(\mathrm{D}), \qquad q = 1 - p\quad(\mathrm{H}).$$

In a random distribution, the molecular fractions of $\mathrm{H_2}$, HD, and $\mathrm{D_2}$ are q^2, $2pq$, and p^2, respectively. Hence,

$$R^{*}_{\mathrm{D_2}} = \frac{p^2}{q^2} = 2.42687372\times 10^{-8}.$$

To account exactly for isotope conservation at $K = 0.300$, let x be the equilibrium mole fraction of $\mathrm{D_2}$, normalizing the total number of molecules to one. Deuterium conservation and normalization give

$$x_{\mathrm{HD}} = 2(p - x), \qquad x_{\mathrm{H_2}} = 1 - 2p + x.$$

Substitution into the equilibrium expression gives

$$0.300 = \frac{x(1 - 2p + x)}{4(p - x)^2}.$$

Equivalently,

$$(1 - 4K)x^2 + (1 - 2p + 8Kp)x - 4Kp^2 = 0.$$

The physically admissible root, $0 \le x \le p$, gives

$$x_{\mathrm{D_2}} = 2.91115995\times 10^{-8},$$
$$x_{\mathrm{HD}} = 3.11461777\times 10^{-4}, \qquad x_{\mathrm{H_2}} = 0.9996885091.$$

Therefore,

$$R_{\mathrm{D_2}} = \frac{x_{\mathrm{D_2}}}{x_{\mathrm{H_2}}} = 2.91206703\times 10^{-8},$$

and

$$\boxed{\Delta_{D_2} = \frac{2.91206703 \times 10^{-8}}{2.42687372 \times 10^{-8}} - 1 = 0.199925\ldots \approx 0.200}.$$

The dilute-deuterium approximation gives the same answer to the appropriate precision:

$$R_{D_2} \approx K\left(\frac{2p}{q}\right)^2 = 4KR^*_{D_2}, \qquad \Delta_{D_2} \approx 4K - 1 = 0.200.$$

2.4

Two printed labels require interpretation. The second carbon-table heading must be ^{13}C, rather than ^{13}O. Also, the measured value must be interpreted as $R_{47} = 4.50865 \times 10^{-5}$, consistent with the instruction "using this R_{47}." The literal alternative is checked below.

Let c_{12}, c_{13} denote the carbon isotope abundances and o_{16}, o_{17}, o_{18} the oxygen isotope abundances.

Carbon dioxide-44 is $^{12}C\,^{16}O_2$, with SMILES `[16O]=[12C]=[16O]`. Its random abundance is

$$P_{44} = c_{12}o_{16}^2.$$

The possible mass-47 carbon dioxide isotopologues are:

Carbon dioxide isotopologue	SMILES	Random abundance
$^{13}C\,^{16}O\,^{18}O$, containing carbon-13, oxygen-16, and oxygen-18	`[16O]=[13C]=[18O]`	$2c_{13}o_{16}o_{18} = 4.43423 \times 10^{-5}$
$^{12}C\,^{17}O\,^{18}O$, containing carbon-12, oxygen-17, and oxygen-18	`[17O]=[12C]=[18O]`	$2c_{12}o_{17}o_{18} = 1.49915 \times 10^{-6}$
$^{13}C\,^{17}O_2$, containing carbon-13 and two oxygen-17 atoms	`[17O]=[13C]=[17O]`	$c_{13}o_{17}^2 = 1.59614 \times 10^{-9}$

These molecules are linear. For different oxygen isotopes, the factor of two counts the two possible assignments to the oxygen positions.

Thus, the most common mass-47 isotopologue is $^{13}C\,^{16}O\,^{18}O$. Retaining only this species as instructed,

$$\begin{aligned} R^*_{47} &= \frac{2c_{13}o_{16}o_{18}}{c_{12}o_{16}^2} \\ &= 2\frac{0.011112}{0.988888}\frac{0.0020000}{0.997621} \\ &= 4.505464112 \times 10^{-5}. \end{aligned}$$

The sample therefore has

$$\Delta_{47} = \frac{4.50865 \times 10^{-5}}{4.505464112 \times 10^{-5}} - 1 = 7.07116413 \times 10^{-4}.$$

Rearranging eq. 11,

$$T = \sqrt{\frac{36.2\ \mathrm{K}^2}{\Delta_{47} - 2.920 \times 10^{-4}}}.$$

Hence,

$$T = \sqrt{\frac{36.2}{7.07116413 \times 10^{-4} - 2.920 \times 10^{-4}}}\ \mathrm{K} = 295.304\ \mathrm{K}.$$

Thus the estimated air temperature is

$$\boxed{T \approx 295.3\ \mathrm{K} \approx 22.2\ ^\circ\mathrm{C}}.$$

If the printed number were instead literally $\Delta_{47} = 4.50865 \times 10^{-5}$, then

$$\Delta_{47} < 2.920 \times 10^{-4},$$

whereas eq. 11 requires $\Delta_{47} > 2.920 \times 10^{-4}$ at every finite positive temperature. That reading therefore yields **no real temperature**.

The solution was checked against the official solution.

Problem 3: Lambert–Beer Law?

In this problem, ignore the absorption of the cell and the solvent. The temperatures of all solutions and gases are kept constant at 25 °C.

PART A

An aqueous solution **X** was prepared using HA and NaA. The concentrations $[\mathrm{A}^-]$, $[\mathrm{HA}]$, and $[\mathrm{H}^+]$ in solution **X** are $1.00 \times 10^{-2}\ \mathrm{mol\,L^{-1}}$, $1.00 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$, and $1.00 \times 10^{-4}\ \mathrm{mol\,L^{-1}}$, respectively, which are correlated via the following acid-base equilibrium:

$$\mathrm{HA} \rightleftharpoons \mathrm{A^-} + \mathrm{H^+} \qquad K = \frac{[\mathrm{A^-}][\mathrm{H^+}]}{[\mathrm{HA}]} \tag{1}$$

The optical path length is l in Part A. Ignore the density change upon dilution. Assume that no chemical reactions other than eq 1 occur.

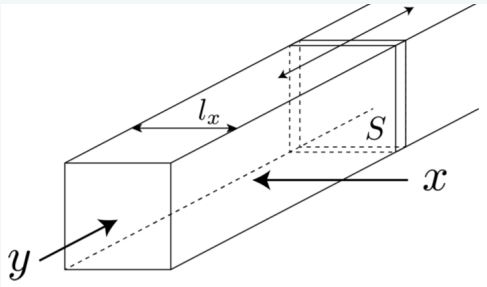
3.1 The absorbance of **X** was A_1 at a wavelength of λ_1. Then, solution **X** was diluted to twice its initial volume using hydrochloric acid with pH = 2.500. After the dilution, the absorbance was still A_1 at λ_1. Determine the ratio $\varepsilon_{\mathrm{HA}}/\varepsilon_{\mathrm{A^-}}$, where $\varepsilon_{\mathrm{HA}}$ and $\varepsilon_{\mathrm{A^-}}$ represent the absorption coefficients of HA and of $\mathrm{A^-}$, respectively, at λ_1.

PART B

Let us consider the following equilibrium in the gas phase:

$$\mathrm{D} \rightleftharpoons 2\mathrm{M} \qquad (2)$$

Pure gas D is filled into a cuboid container that has a transparent movable wall with a cross-section of S (see the figure below) at a pressure P, and equilibrium is established while the total pressure is kept at P. The absorbance of the gas is $A = \varepsilon(n/V)l$, where ε, n, V, and l are the absorption coefficient, amount of the gas in moles, volume of the gas, and optical path length, respectively. Assume that all components of the gas mixture behave as ideal gases.



Use the following definitions if necessary.

	Initial state		After equilibrium	
	D	M	D	M
Partial pressure	P	0	p_D	p_M
Amount in moles	n_0	0	n_D	n_M
Volume	V_0		V	

3.2 The absorbance of the gas at $\lambda_{\mathrm{B}1}$ measured from direction x ($l = l_x$) was $A_{\mathrm{B}1}$ both at the initial state and after the equilibrium. Determine the ratio $\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ at $\lambda_{\mathrm{B}1}$, where ε_D and ε_M represent the absorption coefficients of D and of M, respectively.

3.3 The absorbance of the gas at $\lambda_{\mathrm{B}2}$ measured from direction y was $A_{\mathrm{B}2}$ both at the initial state ($l = l_{y0}$) and after the equilibrium ($l = l_y$). Determine the ratio $\varepsilon_\mathrm{D}/\varepsilon_\mathrm{M}$ at $\lambda_{\mathrm{B}2}$.

Official English text of the problem.

Answers

- **3.1:** $\boxed{\dfrac{\varepsilon_{\mathrm{HA}}}{\varepsilon_{\mathrm{A}^-}} = 8.99}$ at λ_1.
- **3.2:** $\boxed{\dfrac{\varepsilon_\mathrm{D}}{\varepsilon_\mathrm{M}} = 1}$ at $\lambda_{\mathrm{B}1}$.
- **3.3:** $\boxed{\dfrac{\varepsilon_\mathrm{D}}{\varepsilon_\mathrm{M}} = 2}$ at $\lambda_{\mathrm{B}2}$.

Solution

The letter-labelled chemical species are unspecified, so unique molecular names and SMILES cannot be assigned to them. Hydrogen ion H^+ is the proton, `[H+]`.

For a mixture of absorbing species, the individual absorbances add:

$$A = l\sum_i \varepsilon_i c_i.$$

3.1

The acid–base equilibrium is

$$\mathrm{HA} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+.$$

From the initial concentrations,

$$K = \frac{[\mathrm{A}^-][\mathrm{H}^+]}{[\mathrm{HA}]} = \frac{(1.00\times10^{-2})(1.00\times10^{-4})}{1.00\times10^{-3}} = 1.00\times10^{-3}\ \mathrm{mol\,L^{-1}}.$$

The temperature remains constant, so this equilibrium constant also applies after mixing.

The hydrogen-ion concentration of the added hydrochloric acid is

$$[\mathrm{H}^+]_{\mathrm{acid}} = 10^{-2.500}\ \mathrm{mol\,L^{-1}} = 3.16228\times10^{-3}\ \mathrm{mol\,L^{-1}},$$

retaining guard digits for calculation. Doubling the volume requires adding an equal volume of this acid. Dilution alone therefore gives the bookkeeping concentrations

$$
\begin{aligned}
{}_{\text{mix}} &= 5.00 \times 10^{-3}\,\mathrm{mol\,L^{-1}},\\
[\mathrm{HA}]_{\text{mix}} &= 5.00 \times 10^{-4}\,\mathrm{mol\,L^{-1}},\\
[\mathrm{H^+}]_{\text{mix}} &= \frac{1.00 \times 10^{-4} + 3.16228 \times 10^{-3}}{2}\\
&= 1.63114 \times 10^{-3}\,\mathrm{mol\,L^{-1}}.
\end{aligned}
$$

The equilibrium readjusts by protonation:

$$\mathrm{A^-} + \mathrm{H^+} \rightleftharpoons \mathrm{HA}.$$

Let u be the concentration of $\mathrm{A^-}$ protonated. With all concentrations and u expressed in $\mathrm{mol\,L^{-1}}$,

$$
\begin{aligned}
{}_{f} &= 5.00 \times 10^{-3} - u,\\
[\mathrm{HA}]_f &= 5.00 \times 10^{-4} + u,\\
[\mathrm{H^+}]_f &= 1.63114 \times 10^{-3} - u.
\end{aligned}
$$

Substitution into the equilibrium expression gives

$$\frac{(5.00 \times 10^{-3} - u)(1.63114 \times 10^{-3} - u)}{5.00 \times 10^{-4} + u} = 1.00 \times 10^{-3}.$$

Using the unrounded input values, the physically admissible root is

$$u = 1.188237 \times 10^{-3}\,\mathrm{mol\,L^{-1}}.$$

Thus, retaining guard digits,

$$
\begin{aligned}
{}_{f} &= 3.811763 \times 10^{-3}\,\mathrm{mol\,L^{-1}},\\
[\mathrm{HA}]_f &= 1.688237 \times 10^{-3}\,\mathrm{mol\,L^{-1}},\\
[\mathrm{H^+}]_f &= 4.429019 \times 10^{-4}\,\mathrm{mol\,L^{-1}}.
\end{aligned}
$$

Equal absorbance at the same path length requires

$$\varepsilon_{\mathrm{HA}}[\mathrm{HA}]_i + \varepsilon_{\mathrm{A^-}}[\mathrm{A^-}]_i = \varepsilon_{\mathrm{HA}}[\mathrm{HA}]_f + \varepsilon_{\mathrm{A^-}}[\mathrm{A^-}]_f.$$

Consequently,

$$
\begin{aligned}
\frac{\varepsilon_{\mathrm{HA}}}{\varepsilon_{\mathrm{A^-}}} &= \frac{[\mathrm{A^-}]_i - [\mathrm{A^-}]_f}{[\mathrm{HA}]_f - [\mathrm{HA}]_i}\\
&= \frac{1.00 \times 10^{-2} - 3.811763 \times 10^{-3}}{1.688237 \times 10^{-3} - 1.00 \times 10^{-3}}\\
&= 8.99143\ldots\\
&= \boxed{8.99}.
\end{aligned}
$$

3.2

The gas-phase equilibrium is

$$\mathrm{D} \rightleftharpoons 2\,\mathrm{M}.$$

In direction x, the optical path length l_x is fixed. Initially, the ideal-gas equation gives

$$\frac{n_0}{V_0} = \frac{P}{RT},$$

so the initial absorbance is

$$A_{\mathrm{B1},i} = \varepsilon_{\mathrm{D}} \frac{P}{RT} l_x.$$

At equilibrium,

$$A_{\mathrm{B1},f} = \Big(\varepsilon_{\mathrm{D}} \frac{p_{\mathrm{D}}}{RT} + \varepsilon_{\mathrm{M}} \frac{p_{\mathrm{M}}}{RT}\Big) l_x.$$

Equating the absorbances and cancelling $l_x/(RT)$ gives

$$\varepsilon_{\mathrm{D}} P = \varepsilon_{\mathrm{D}} p_{\mathrm{D}} + \varepsilon_{\mathrm{M}} p_{\mathrm{M}}.$$

Since the total pressure remains P,

$$P = p_{\mathrm{D}} + p_{\mathrm{M}}.$$

Hence,

$$(\varepsilon_{\mathrm{D}} - \varepsilon_{\mathrm{M}}) p_{\mathrm{M}} = 0.$$

The dissociation produces a nonzero amount of M, so

$$\boxed{\frac{\varepsilon_{\mathrm{D}}}{\varepsilon_{\mathrm{M}}} = 1}.$$

At constant pressure and temperature, the total molar concentration stays constant. Equal absorption coefficients therefore give unchanged absorbance along the fixed path.

3.3

In direction y, the path length changes as the movable wall moves. The cross-sectional area S is fixed, giving

$$V_0 = S l_{y0}, \qquad V = S l_y.$$

The initial absorbance is therefore

$$A_{\mathrm{B2},i} = \varepsilon_{\mathrm{D}} \frac{n_0}{V_0} l_{y0} = \frac{\varepsilon_{\mathrm{D}} n_0}{S}.$$

At equilibrium,

$$\begin{aligned} A_{\mathrm{B2},f} &= \left(\varepsilon_{\mathrm{D}} \frac{n_{\mathrm{D}}}{V} + \varepsilon_{\mathrm{M}} \frac{n_{\mathrm{M}}}{V}\right) l_y \\ &= \frac{\varepsilon_{\mathrm{D}} n_{\mathrm{D}} + \varepsilon_{\mathrm{M}} n_{\mathrm{M}}}{S}. \end{aligned}$$

Equal absorbance thus requires

$$\varepsilon_{\mathrm{D}} n_0 = \varepsilon_{\mathrm{D}} n_{\mathrm{D}} + \varepsilon_{\mathrm{M}} n_{\mathrm{M}}.$$

From the stoichiometry of $\mathrm{D} \rightleftharpoons 2\,\mathrm{M}$,

$$n_0 = n_{\mathrm{D}} + \frac{n_{\mathrm{M}}}{2}.$$

Substituting this balance gives

$$\varepsilon_{\mathrm{D}} \left(n_{\mathrm{D}} + \frac{n_{\mathrm{M}}}{2}\right) = \varepsilon_{\mathrm{D}} n_{\mathrm{D}} + \varepsilon_{\mathrm{M}} n_{\mathrm{M}},$$

and therefore

$$\left(\frac{\varepsilon_{\mathrm{D}}}{2} - \varepsilon_{\mathrm{M}}\right) n_{\mathrm{M}} = 0.$$

Since $n_{\mathrm{M}} > 0$,

$$\boxed{\frac{\varepsilon_{\mathrm{D}}}{\varepsilon_{\mathrm{M}}} = 2}.$$

Along this direction, $l_y/V = 1/S$, so each mole of D must absorb as much as the two moles of M formed from it.

The solution was checked against the official solution.

Problem 4: The Redox Chemistry of Zinc



Zinc has long been used as alloys for brass and steel materials. The zinc contained in industrial wastewater is separated by precipitation to detoxify the water, and the obtained precipitate is reduced to recover and reuse it as metallic zinc.

PART A

The dissolution equilibrium of zinc hydroxide $\mathrm{Zn(OH)_2\,(s)}$ at 25 °C and the relevant equilibrium constants are given in eq. 1–4.

$$\mathrm{Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)} \qquad K_{sp} = 1.74 \times 10^{-17} \tag{1}$$

$$\mathrm{Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq)} \qquad K_1 = 2.62 \times 10^{-6} \tag{2}$$

$$\mathrm{Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)} \qquad K_2 = 6.47 \times 10^{-2} \tag{3}$$

$$\mathrm{H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)} \qquad K_w = 1.00 \times 10^{-14} \tag{4}$$

The solubility, S, of zinc (concentration of zinc in a saturated aqueous solution) is given in eq. 5.

$$S = [\mathrm{Zn^{2+}\,(aq)}] + [\mathrm{Zn(OH)_2\,(aq)}] + [\mathrm{Zn(OH)_4{}^{2-}\,(aq)}] \tag{5}$$

4.1 When the equilibria in eq. 1–4 are established, calculate the pH range in which $[\mathrm{Zn(OH)_2\,(aq)}]$ is the greatest among $[\mathrm{Zn^{2+}\,(aq)}]$, $[\mathrm{Zn(OH)_2\,(aq)}]$ and $[\mathrm{Zn(OH)_4{}^{2-}\,(aq)}]$.

4.2 A saturated aqueous solution of $\mathrm{Zn(OH)_2\,(s)}$ with pH = 7.00 was prepared and filtered. NaOH was added to this filtrate to increase its pH to 12.00. Calculate the molar percentage of zinc that precipitates when increasing the pH from 7.00 to 12.00. Ignore the volume and temperature changes.

PART B

Next, the recovered zinc hydroxide is heated to obtain zinc oxide according to the reaction below:

$$\mathrm{Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O(l)} \tag{6}$$

The zinc oxide is then reduced to metallic zinc by reaction with hydrogen:

$$\mathrm{ZnO(s) + H_2(g) \rightarrow Zn(s) + H_2O(g)} \tag{7}$$

4.3 In order for reaction (7) to proceed at a hydrogen pressure kept at 1 bar, it is necessary to reduce the partial pressure of the generated water vapor. Calculate the upper limit for the partial pressure of water vapor to allow reaction (7) to proceed at 300 °C. Here, the Gibbs formation energies of zinc oxide and water vapor at 300 °C and 1 bar for all gaseous species are $\Delta G_{\mathrm{ZnO}}(300\,^\circ\mathrm{C}) = -2.90 \times 10^2\ \mathrm{kJ\,mol^{-1}}$ and $\Delta G_{\mathrm{H_2O}}(300\,^\circ\mathrm{C}) = -2.20 \times 10^2\ \mathrm{kJ\,mol^{-1}}$, respectively.

Metallic zinc is used as a negative electrode (anode) material for metal-air batteries. The electrode consists of Zn and ZnO. It uses the following redox reaction to generate electricity with the electromotive force (e.m.f.) at 25 °C and pressure of 1 bar, E°.

$$\mathrm{Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)} \qquad E^\circ = 1.65\,\mathrm{V} \tag{8}$$

4.4 A zinc–air battery was discharged at 20 mA for 24 hours. Calculate the change in mass of the negative electrode (anode) of the battery.



Mt. Fuji

4.5 Consider the change of e.m.f. of a zinc–air battery depending on the environment. **Calculate** the e.m.f. at the summit of Mt. Fuji, where the temperature and altitude are −38 °C (February) and 3776 m, respectively. The atmospheric pressure is represented by

$$P\,[\mathrm{bar}] = 1.013 \times \left(1 - \frac{0.0065h}{T + 0.0065h + 273.15}\right)^{5.257} \tag{9}$$

at altitude h [m] and temperature T [°C]. The molar ratio of oxygen in the atmosphere is 21%. The Gibbs energy change of reaction (8) is $\Delta G_{\mathrm{ZnO}}(-38\,^\circ\mathrm{C}) = -3.26 \times 10^2\ \mathrm{kJ\,mol^{-1}}$ at −38 °C and 1 bar.

4.6 Calculate the Gibbs energy change for reaction (6) at 25 °C. Note that the standard reduction potentials, $E^\circ(\mathrm{Zn^{2+}/Zn})$ and $E^\circ(\mathrm{O_2/H_2O})$ at 25 °C and 1 bar are given as (10) and (11), respectively.

$$\mathrm{Zn^{2+} + 2e^- \rightarrow Zn} \qquad E^\circ(\mathrm{Zn^{2+}/Zn}) = -0.77\,\mathrm{V} \tag{10}$$

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O} \qquad E^\circ(\mathrm{O_2/H_2O}) = 1.23\,\mathrm{V} \tag{11}$$

Official English text of the problem.

Answers

- **4.1:** $\boxed{8.41 \le \mathrm{pH} \le 11.80}$. The dissolved neutral species is strictly most abundant between the boundaries; it ties with another species at each boundary.
- **4.2:** $\boxed{99.48\%}$ of the zinc precipitates.
- **4.3:** The limiting water-vapor pressure is $\boxed{4.2 \times 10^{-7}\ \mathrm{bar}}$. Forward reduction requires a pressure below this limit.
- **4.4:** $\boxed{\Delta m = +0.143\ \mathrm{g}}$: the anode gains mass.
- **4.5:** $\boxed{E = 1.68\ \mathrm{V}}$.
- **4.6:** $\boxed{\Delta_\mathrm{r}G^\circ = +3.38\ \mathrm{kJ\,mol^{-1}}}$.

Solution

Use $R = 8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$, $F = 96485\ \mathrm{C\,mol^{-1}}$, and $M(\mathrm{O}) = 16.00\ \mathrm{g\,mol^{-1}}$. Pure solids and liquid water have unit activity; gas activities are p/p°, with $p^\circ = 1\ \mathrm{bar}$.

Species names and SMILES used below are zinc(II) ion `[Zn+2]`, hydroxide ion `[OH-]`, hydrogen ion `[H+]`, water `O`, hydrogen `[H][H]`, oxygen `O=O`, and sodium hydroxide `[Na+].[OH-]`. Dissolved zinc hydroxide can be represented by the dative-bond SMILES `[OH-]->[Zn+2]<-[OH-]`, and tetrahydroxozincate(II) by `[OH-]->[Zn+2](<-[OH-])(<-[OH-])<-[OH-]`. These representations omit solvent coordination and do not encode the tetrahedral coordination geometry of tetrahydroxozincate. The solid phases have extended structures rather than unique molecular SMILES.

4.1

Let

$$x = \frac{[\mathrm{OH^-}]}{c^\circ}, \qquad c^\circ = 1\ \mathrm{mol\,L^{-1}}.$$

The three dissolution equilibria give

$$\frac{[\mathrm{Zn^{2+}}]}{c^\circ} = \frac{K_{\mathrm{sp}}}{x^2}, \qquad \frac{[\mathrm{Zn(OH)_2}]}{c^\circ} = K_1, \qquad \frac{[\mathrm{Zn(OH)_4{}^{2-}}]}{c^\circ} = K_2 x^2,$$

where

$$K_{\mathrm{sp}} = 1.74 \times 10^{-17}, \quad K_1 = 2.62 \times 10^{-6}, \quad K_2 = 6.47 \times 10^{-2}.$$

For the neutral dissolved species to have the greatest concentration, both conditions must hold:

$$K_1 \geq \frac{K_{\mathrm{sp}}}{x^2}, \qquad K_1 \geq K_2 x^2.$$

Therefore,

$$\sqrt{\frac{K_{\mathrm{sp}}}{K_1}} \leq x \leq \sqrt{\frac{K_1}{K_2}},$$

or

$$2.577 \times 10^{-6} \leq x \leq 6.364 \times 10^{-3}.$$

Since $K_{\mathrm{w}} = 1.00 \times 10^{-14}$,

$$\mathrm{pH} = 14.00 + \log_{10} x.$$

Thus,

$$\boxed{8.41 \leq \mathrm{pH} \leq 11.80}.$$

At the lower boundary, $[\mathrm{Zn(OH)_2}] = [\mathrm{Zn^{2+}}]$; at the upper boundary, $[\mathrm{Zn(OH)_2}] = [\mathrm{Zn(OH)_4{}^{2-}}]$. Strict dominance holds inside the interval.

4.2

The total dissolved zinc concentration at saturation is

$$S = c^\circ \left(\frac{K_{\mathrm{sp}}}{x^2} + K_1 + K_2 x^2 \right).$$

At pH 7.00, $x = 10^{-7}$, so

$$\begin{aligned} S_7 &= \left(\frac{1.74 \times 10^{-17}}{10^{-14}} + 2.62 \times 10^{-6} + (6.47 \times 10^{-2})(10^{-14}) \right) \mathrm{mol\,L^{-1}} \\ &= 1.74262 \times 10^{-3}\ \mathrm{mol\,L^{-1}}. \end{aligned}$$

At pH 12.00, $x = 10^{-2}$, giving

$$\begin{aligned} S_{12} &= \left(\frac{1.74 \times 10^{-17}}{10^{-4}} + 2.62 \times 10^{-6} + (6.47 \times 10^{-2})(10^{-4}) \right) \mathrm{mol\,L^{-1}} \\ &= 9.09000 \times 10^{-6}\ \mathrm{mol\,L^{-1}}. \end{aligned}$$

Precipitation occurs principally through

$$\mathrm{Zn^{2+}\,(aq) + 2\,OH^-\,(aq) \longrightarrow Zn(OH)_2\,(s)}.$$

Because the volume is unchanged, the fraction precipitated is the decrease in dissolved concentration divided by its initial value:

$$\begin{aligned} \%\ \text{precipitated} &= 100 \left(1 - \frac{S_{12}}{S_7} \right) \\ &= 100 \left(1 - \frac{9.09000 \times 10^{-6}}{1.74262 \times 10^{-3}} \right) \\ &= \boxed{99.48\%}. \end{aligned}$$

This includes zinc remaining dissolved as tetrahydroxozincate at the final pH.

4.3

For

$$\mathrm{ZnO\,(s) + H_2\,(g) \longrightarrow Zn\,(s) + H_2O\,(g)},$$

the standard Gibbs energy change at $300\ ^\circ\mathrm{C}$ is

$$\begin{aligned} \Delta_{\mathrm{r}} G^\circ &= \Delta_{\mathrm{f}} G^\circ(\mathrm{H_2O\,(g)}) - \Delta_{\mathrm{f}} G^\circ(\mathrm{ZnO\,(s)}) \\ &= (-220) - (-290) \\ &= +70.0\ \mathrm{kJ\,mol^{-1}}. \end{aligned}$$

The elemental substances have zero standard Gibbs energies of formation. The reaction quotient is

$$Q = \frac{p_{\mathrm{H_2O}}/p^\circ}{p_{\mathrm{H_2}}/p^\circ} = \frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}}.$$

At the limiting pressure, $\Delta_\mathrm{r}G = 0$:

$$0 = \Delta_\mathrm{r}G^\circ + RT\ln Q.$$

Using $T = 573.15\ \mathrm{K}$ and $p_{\mathrm{H_2}} = 1\ \mathrm{bar}$,

$$\begin{aligned} p_{\mathrm{H_2O,lim}} &= (1\ \mathrm{bar})\exp\left(-\frac{70000}{8.314(573.15)}\right) \\ &= 4.17\times10^{-7}\ \mathrm{bar}. \end{aligned}$$

Hence forward reduction requires

$$\boxed{p_{\mathrm{H_2O}} < 4.2\times10^{-7}\ \mathrm{bar}}.$$

Equality corresponds to equilibrium.

4.4

The overall discharge reaction is

$$\mathrm{Zn\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{ZnO\,(s)}.$$

Zinc changes oxidation state from 0 to $+2$, so each mole of zinc converted transfers two moles of electrons.

The charge passed is

$$Q = It = (0.020\ \mathrm{A})(24\times3600\ \mathrm{s}) = 1728\ \mathrm{C}.$$

Thus,

$$n_{\mathrm{Zn,converted}} = \frac{Q}{2F} = \frac{1728}{2(96485)} = 8.955\times10^{-3}\ \mathrm{mol}.$$

The electrode contains both zinc and zinc oxide. Zinc remains in the electrode, while one oxygen atom is incorporated per zinc atom oxidized. Therefore,

$$\begin{aligned} \Delta m &= n_{\mathrm{Zn,converted}}\left[M(\mathrm{ZnO}) - M(\mathrm{Zn})\right] \\ &= n_{\mathrm{Zn,converted}}M(\mathrm{O}) \\ &= (8.955\times10^{-3})(16.00) \\ &= \boxed{+0.143\ \mathrm{g}}. \end{aligned}$$

The anode gains mass.

4.5

First calculate the atmospheric pressure:

$$\begin{aligned} P &= 1.013\left(1 - \frac{0.0065(3776)}{-38 + 0.0065(3776) + 273.15}\right)^{5.257}\ \mathrm{bar} \\ &= 0.6011\ \mathrm{bar}. \end{aligned}$$

The oxygen partial pressure is therefore

$$p_{\mathrm{O_2}} = 0.21P = 0.1262\ \mathrm{bar}.$$

At $-38\ ^\circ\mathrm{C}$, $T = 235.15\ \mathrm{K}$. Obtain the standard e.m.f. at this temperature from the supplied Gibbs energy:

$$E^\circ(T) = -\frac{\Delta_\mathrm{r}G^\circ(T)}{2F} = \frac{326000}{2(96485)} = 1.6894\ \mathrm{V}.$$

For

$$\mathrm{Zn\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{ZnO\,(s)},$$

the reaction quotient is

$$Q = \left(\frac{p_{\mathrm{O_2}}}{p^\circ}\right)^{-1/2}.$$

The Nernst equation consequently gives

$$\begin{aligned} E &= E^\circ(T) - \frac{RT}{2F}\ln Q \\ &= E^\circ(T) + \frac{RT}{4F}\ln\left(\frac{p_{\mathrm{O_2}}}{p^\circ}\right) \\ &= 1.6894 + \frac{8.314(235.15)}{4(96485)}\ln(0.1262) \\ &= 1.6789\ \mathrm{V}. \end{aligned}$$

Thus,

$$\boxed{E = 1.68\ \mathrm{V}}.$$

4.6

The target reaction is

$$\mathrm{Zn(OH)_2\,(s)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{H_2O\,(l)}.$$

Construct a Hess cycle at $25\ ^\circ\mathrm{C}$.

First, combine zinc oxidation with oxygen reduction:

$$\begin{gathered}\mathrm{Zn\,(s)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + 2\,\mathrm{e^-}, \\ \tfrac{1}{2}\,\mathrm{O_2\,(g)} + 2\,\mathrm{H^+\,(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2O\,(l)}.\end{gathered}$$

Their sum is

$$\mathrm{Zn\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} + 2\,\mathrm{H^+\,(aq)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + \mathrm{H_2O\,(l)}. \qquad \text{(A)}$$

The cell potential and corresponding Gibbs energy are

$$\begin{aligned}E_A^\circ &= 1.23 - (-0.77) = 2.00\ \mathrm{V}, \\ \Delta G_A^\circ &= -2FE_A^\circ = -385.94\ \mathrm{kJ\,mol^{-1}}.\end{aligned}$$

Next, combine dissolution,

$$\mathrm{Zn(OH)_2\,(s)} \rightleftharpoons \mathrm{Zn^{2+}\,(aq)} + 2\,\mathrm{OH^-\,(aq)},$$

with neutralization,

$$2\,\mathrm{H^+\,(aq)} + 2\,\mathrm{OH^-\,(aq)} \longrightarrow 2\,\mathrm{H_2O\,(l)}.$$

The resulting reaction is

$$\mathrm{Zn(OH)_2\,(s)} + 2\,\mathrm{H^+\,(aq)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + 2\,\mathrm{H_2O\,(l)}. \qquad \text{(B)}$$

Its equilibrium constant is

$$K_B = \frac{K_{\mathrm{sp}}}{K_{\mathrm{w}}^2} = \frac{1.74 \times 10^{-17}}{(1.00 \times 10^{-14})^2} = 1.74 \times 10^{11}.$$

Therefore,

$$\begin{aligned}\Delta G_B^\circ &= -RT \ln K_B \\ &= -8.314(298.15) \ln(1.74 \times 10^{11}) \\ &= -64.16\ \mathrm{kJ\,mol^{-1}}.\end{aligned}$$

Finally, reaction (8) is

$$\mathrm{Zn\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{ZnO\,(s)},$$

with

$$\Delta G_8^\circ = -2F(1.65) = -318.40\ \mathrm{kJ\,mol^{-1}}.$$

Adding reaction (B), the reverse of reaction (A), and reaction (8) cancels the ions, oxygen, and metallic zinc, leaving exactly

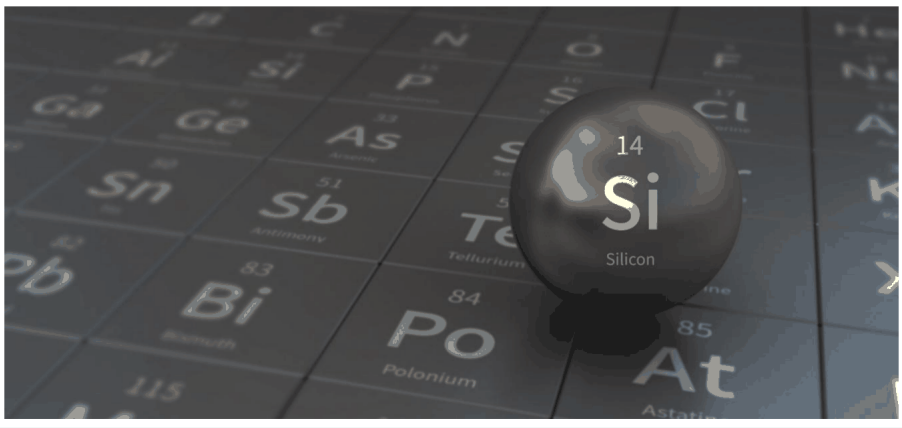
$$\mathrm{Zn(OH)_2\,(s)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{H_2O\,(l)}.$$

Hence,

$$\begin{aligned}\Delta G_6^\circ &= \Delta G_B^\circ - \Delta G_A^\circ + \Delta G_8^\circ \\ &= -64.16 - (-385.94) - 318.40 \\ &= \boxed{+3.38\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

The solution was checked against the official solution.

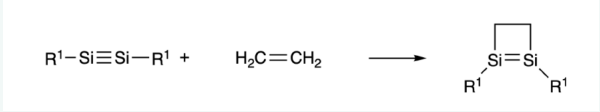
Problem 5: Mysterious Silicon



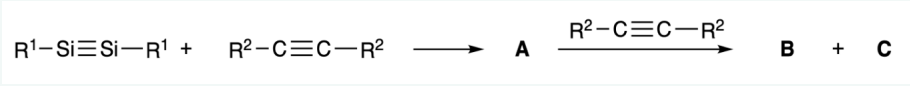
Although silicon is also a group 14 element like carbon, their properties differ significantly.

PART A

Unlike the carbon–carbon triple bond, the silicon–silicon triple bond in a compound formulated as $\mathrm{R^1{-}Si{\equiv}Si{-}R^1}$ (R: organic substituent) is extremely reactive. For example, it reacts with ethylene to form a cyclic product that contains a four-membered ring.



When $R^1-Si\equiv Si-R^1$ is treated with an alkyne ($R^2-C\equiv C-R^2$), the four-membered-ring compound **A** is formed as an initial intermediate. Further reaction of another molecule of $R^2-C\equiv C-R^2$ with **A** affords isomers **B** and **C**, both of which have benzene-like cyclic conjugated structures, so-called 'disilabenzenes' that contain a six-membered ring and can be formulated as $(R^1-Si)_2(R^2-C)_4$.



The ^{13}C NMR analysis of the corresponding six-membered ring skeletons Si_2C_4 shows two signals for **B** and one signal for **C**.

5.1 Draw the structural formulae of **A**, **B**, and **C** using R^1, R^2, Si, and C, with one of the possible resonance structures.

5.2 Calculate the aromatic stabilization energy (ASE) for benzene and **C** (in the case of $R^1 = R^2 = H$) as positive values, considering the enthalpy change in some hydrogenation reactions of unsaturated systems shown below (Fig. 1).

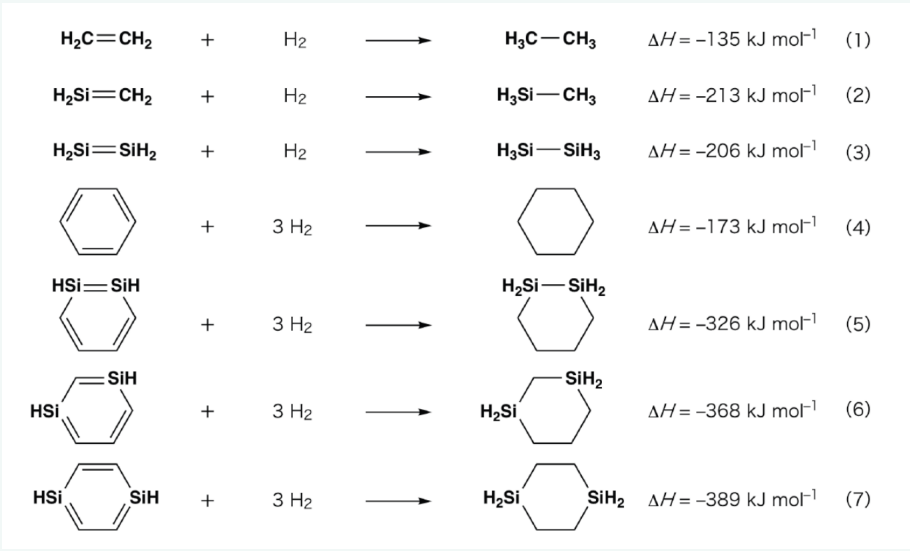


Fig. 1

When a xylene solution of **C** is heated, it undergoes isomerization to give an equilibrium mixture of compounds **D** and **E**. The molar ratio is **D : E** = 1 : 40.0 at 50.0 °C and **D : E** = 1 : 20.0 at 120.0 °C.

5.3 Calculate ΔH for the transformation of **D** to **E**. Assume that ΔH does not depend on temperature.

The isomerization from **C** to **D** and to **E** proceeds via transformations of π-bonds into σ-bonds without breaking any σ-bonds. A ^{13}C NMR analysis revealed one signal for the Si_2C_4 skeleton of **D** and two signals for that of **E**. The skeleton of **D** does not contain any three-membered rings, while **E** has two three membered rings that share an edge.

5.4 Draw the structural formulae of **D** and **E** using R^1, R^2, Si, and C

PART B

Silicon is able to form highly coordinated compounds (> four substituents) with electronegative elements such as fluorine. As metal fluorides are often used as fluorination reagents, highly coordinated silicon fluorides also act as fluorination reagents.

The fluorination reaction of CCl_4 using Na_2SiF_6 was carried out as follows.

Standardization of Na_2SiF_6 solution:

- Preparation

Aqueous solution **F**: 0.855 g of Na_2SiF_6 (188.053 g mol^{-1}) dissolved in water (total volume: 200 mL).

Aqueous solution **G**: 6.86 g of $Ce_2(SO_4)_3$ (568.424 g mol^{-1}) dissolved in water (total volume: 200 mL).

- Procedure

Precipitation titration of a solution **F** (50.0 mL) by dropwise adding solution **G** in the presence of xylenol orange, which coordinates to Ce^{3+}, as an indicator. After adding 18.8 mL of solution **G**, the color of the solution changes from yellow to magenta. The generated precipitate is a binary compound that contains Ce^{3+}, and the only resulting silicon compound is $Si(OH)_4$.

5.5 Write the balanced equation for the reaction of Na_2SiF_6 with $Ce_2(SO_4)_3$.

- Reaction of CCl_4 with Na_2SiF_6:

(Substance losses by *e.g.* evaporation are negligible during the following operations.)

$\mathrm{Na_2SiF_6}$(x [g]) was added to $\mathrm{CCl_4}$ (500.0 g) and heated to 300°C in a sealed pressure-resistant reaction vessel. The unreacted $\mathrm{Na_2SiF_6}$ and generated NaCl were removed by filtration. The filtrate was diluted to a total volume of 1.00 L with $\mathrm{CCl_4}$ (solution **H**). The $^{29}\mathrm{Si}$ and $^{19}\mathrm{F}$ NMR spectra of solution **H** showed $\mathrm{SiF_4}$ as the only silicon compound. In the $^{19}\mathrm{F}$ NMR spectrum, in addition to $\mathrm{SiF_4}$, signals corresponding to $\mathrm{CFCl_3}$, $\mathrm{CF_2Cl_2}$, $\mathrm{CF_3Cl}$, and $\mathrm{CF_4}$ were observed (cf. Table 1). The integration ratios in the $^{19}\mathrm{F}$ NMR spectrum are proportional to the number of fluorine nuclei.

Table 1

$^{19}\mathrm{F}$ NMR data	$\mathrm{CFCl_3}$	$\mathrm{CF_2Cl_2}$	$\mathrm{CF_3Cl}$	$\mathrm{CF_4}$
Integration ratio	45.0	65.0	18.0	2.0

$\mathrm{SiF_4}$ is hydrolyzed to form $\mathrm{H_2SiF_6}$ according to the following eq. 8:

$$3\mathrm{SiF_4} + 2\mathrm{H_2O} \rightarrow \mathrm{SiO_2} + 2\mathrm{H_2SiF_6} \qquad (8)$$

Solution **H** (10 mL) was added to an excess amount of water, which resulted in the complete hydrolysis of $\mathrm{SiF_4}$. After separation, the $\mathrm{H_2SiF_6}$ generated from the hydrolysis in the aqueous solution was neutralized and completely converted to $\mathrm{Na_2SiF_6}$ (aqueous solution **J**).

The precipitate of unreacted $\mathrm{Na_2SiF_6}$ and NaCl, which was removed by filtration in the initial step (underlined), was completely dissolved in water to give an aqueous solution (solution **K**; 10.0 L).

Then, additional precipitation titrations using solution **G** were carried out, and the endpoints of the titrations with **G** were as follows:

- For solution **J** (entire amount): 61.6 mL.
- For 100 mL of solution **K**: 44.4 mL.

It should be noted here that the coexistence of NaCl or $\mathrm{SiO_2}$ has no effect on the precipitation titration.

5.6 Calculate the mass of the NaCl produced in the reaction vessel (information underlined), and calculate the mass (x [g]) of the $\mathrm{Na_2SiF_6}$ used as a starting material.

5.7 77.8% of the $\mathrm{CCl_4}$ used as a starting material was unreacted. **Calculate** the mass of $\mathrm{CF_3Cl}$ generated.

Official English text of the problem.

Answers

In the generic SMILES below, each `[*:1]` represents an $\mathrm{R^1}$ substituent and each `[*:2]` an $\mathrm{R^2}$ substituent. The names identify the parent skeletons. Stereochemical marks in **D** and **E** specify their relative cage arrangements; they do not specify stereochemistry within the R groups.

- **5.1**
- **A:** substituted **1,2-disilacyclobuta-1,3-diene**, `[*:1][Si]1=[Si]([*:1])C([*:2])=C1[*:2]`.
- **B:** substituted **1,2-disilabenzene**, `[*:1][Si]1=[Si]([*:1])C([*:2])=C([*:2])C([*:2])=C1[*:2]`.
- **C:** substituted **1,4-disilabenzene**, `[*:1][Si]1=C([*:2])C([*:2])=[Si]([*:1])C([*:2])=C1[*:2]`.
- **5.2** Benzene, `c1ccccc1`: $\boxed{\mathrm{ASE} = 232\ \mathrm{kJ\,mol^{-1}}}$.
  C, with $\mathrm{R^1} = \mathrm{R^2} = \mathrm{H}$: $\boxed{\mathrm{ASE} = 172\ \mathrm{kJ\,mol^{-1}}}$.
- **5.3** $\boxed{\Delta H_{\mathrm{D}\rightarrow\mathrm{E}} = -10.5\ \mathrm{kJ\,mol^{-1}}}$.
- **5.4**
- **D:** substituted **1,4-disilabicyclo[2.2.0]hexa-2,5-diene**, the disila-Dewar benzene structure, `[*:1][Si@]12C([*:2])=C([*:2])[Si@@]1([*:1])C([*:2])=C2[*:2]`.
- **E:** substituted **2,5-disilabenzvalene**, `[*:1][Si@@]12[C@@]3([*:2])[C@]1([*:2])[Si@@]3([*:1])C([*:2])=C2[*:2]`.
- **5.5**

$$\boxed{\mathrm{Na_2SiF_6} + \mathrm{Ce_2(SO_4)_3} + 4\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{CeF_3\,(s)} + \mathrm{Si(OH)_4} + \mathrm{Na_2SO_4} + 2\,\mathrm{H_2SO_4}}$$

- **5.6** Sodium chloride, `[Na+].[Cl-]`: $\boxed{65.2\ \mathrm{g}}$.
  Starting sodium hexafluorosilicate, `[Na+].[Na+].F[Si-2](F)(F)(F)(F)F`: $\boxed{x = 155\ \mathrm{g}}$.
- **5.7** Chlorotrifluoromethane, `FC(F)(F)Cl`: $\boxed{5.38\ \mathrm{g}}$.

Solution

5.1 — Structures of A, B, and C

The reaction with ethylene shows that cycloaddition consumes one of the two π-bonds of the silicon–silicon triple bond. With an alkyne, one π-bond from each triple bond is consumed, leaving a four-membered ring with opposite $\mathrm{Si{=}Si}$ and $\mathrm{C{=}C}$ bonds.

Thus, to draw **A**, place two adjacent silicon atoms along one edge of a square and two carbon atoms along the opposite edge. Draw both these edges as double bonds and the other two edges as single bonds. Each silicon carries $\mathrm{R^1}$, and each carbon carries $\mathrm{R^2}$.

For the six-membered conjugated products, the possible relative silicon positions give the following carbon environments:

Silicon positions	Equivalent carbon positions	Number of $^{13}\mathrm{C}$ signals
1,2	$3 \equiv 6;\ 4 \equiv 5$	2

Silicon positions	Equivalent carbon positions	Number of $^{13}\mathrm{C}$ signals
1,3	$2;\ 5;\ 4 \equiv 6$	3
1,4	$2 \equiv 3 \equiv 5 \equiv 6$	1

The observed two signals therefore identify **B** as the **1,2-disilabenzene**, while one signal identifies **C** as the **1,4-disilabenzene**.

Precise drawings corresponding to the SMILES in the answers are:

- **B:** a six-membered ring numbered consecutively, with silicon at positions 1 and 2 and carbon at positions 3–6. Draw double bonds $1 = 2$, $3 = 4$, and $5 = 6$.
- **C:** a six-membered ring with silicon at positions 1 and 4. Draw double bonds $1 = 2$, $3 = 4$, and $5 = 6$.

Attach R^1 to every silicon and R^2 to every carbon. These are individual Kekulé contributors; the NMR equivalence concerns the conjugated molecules.

5.2 — Aromatic stabilization energies

The isolated-double-bond references are ethene, `C=C`, for $\mathrm{C{=}C}$, and silene, `C=[SiH2]`, for $\mathrm{Si{=}C}$.

The positive stabilization energy is the difference between the actual hydrogenation enthalpy and the sum expected for isolated double bonds:

$$\mathrm{ASE} = \Delta H_{\mathrm{hyd,actual}} - \sum \Delta H_{\mathrm{hyd,isolated}}.$$

For **benzene**, the isolated-bond reference contains three $\mathrm{C{=}C}$ bonds:

$$\Delta H_{\mathrm{hyd,reference}} = 3(-135) = -405\ \mathrm{kJ\,mol^{-1}}.$$

Using reaction (4),

$$\boxed{\mathrm{ASE_{benzene}} = -173 - (-405) = 232\ \mathrm{kJ\,mol^{-1}}}.$$

For **C** with hydrogen substituents, the molecule is **1,4-disilabenzene**, `[SiH]1=CC=[SiH]C=C1`. A Kekulé structure contains two $\mathrm{Si{=}C}$ bonds and one $\mathrm{C{=}C}$ bond:

$$\Delta H_{\mathrm{hyd,reference}} = 2(-213) + (-135) = -561\ \mathrm{kJ\,mol^{-1}}.$$

The opposite silicon positions identify its hydrogenation as reaction (7), with $\Delta H = -389\ \mathrm{kJ\,mol^{-1}}$. Hence,

$$\boxed{\mathrm{ASE_C} = -389 - (-561) = 172\ \mathrm{kJ\,mol^{-1}}}.$$

5.3 — Enthalpy change for D to E

For the equilibrium $\mathrm{D} \rightleftharpoons \mathrm{E}$,

$$K = \frac{[\mathrm{E}]}{[\mathrm{D}]}.$$

Thus,

$$K_1 = 40.0, \quad T_1 = 323.15\ \mathrm{K}, \qquad K_2 = 20.0, \quad T_2 = 393.15\ \mathrm{K}.$$

The integrated van 't Hoff equation is

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

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

$$\Delta H = -\frac{8.314 \ln(20.0/40.0)}{1/393.15 - 1/323.15} = -1.046 \times 10^4\ \mathrm{J\,mol^{-1}}.$$

Therefore,

$$\boxed{\Delta H_{\mathrm{D\to E}} = -10.5\ \mathrm{kJ\,mol^{-1}}}.$$

The exothermic sign agrees with the greater proportion of **E** at the lower temperature.

5.4 — Structures of D and E

Retain the numbering of **C**:

$$\mathrm{Si_1 - C_2 - C_3 - Si_4 - C_5 - C_6 - Si_1}.$$

Every edge in this original six-membered ring must remain as a σ-bond. Silicon atoms retain their R^1 substituents and carbon atoms their R^2 substituents.

For **D**, add a single bond between silicon atoms 1 and 4. The remaining double bonds are $2 = 3$ and $5 = 6$.

This gives two four-membered rings:

$$(1, 2, 3, 4), \qquad (1, 4, 5, 6),$$

sharing the $\mathrm{Si{-}Si}$ edge. There are no three-membered rings. Symmetry makes all four carbon atoms equivalent, giving the required one carbon signal.

Thus **D** is the **disila-Dewar benzene** structure. Draw the two four-membered rings folded about their shared silicon–silicon bond; the molecular framework is not planar.

For **E**, add single bonds $1 - 3$ and $2 - 4$, and retain only the double bond $5 = 6$.

The resulting three-membered rings are

$$(1, 2, 3), \qquad (2, 3, 4),$$

which share the carbon–carbon edge $2 - 3$. The carbon environments are:

- the two equivalent saturated carbons, 2 and 3;
- the two equivalent alkene carbons, 5 and 6.

This gives the required two carbon signals. **E** is therefore **2,5-disilabenzvalene**. Draw the two $\mathrm{SiC_2}$ triangles sharing their carbon–carbon edge, with the two silicon vertices also connected through the $\mathrm{C{=}C}$-containing path $1-6=5-4$. This is a folded cage structure.

Both constructions preserve all six original ring σ-bonds and satisfy the valence of every skeletal atom.

5.5 — Precipitation reaction

The amount of sodium hexafluorosilicate in the titrated portion of **F** is

$$n_F = \frac{0.855\ \mathrm{g}}{188.053\ \mathrm{g\,mol^{-1}}}\frac{50.0}{200} = 1.13665\times10^{-3}\ \mathrm{mol}.$$

The amount of cerium(III) supplied at the endpoint is

$$n_{\mathrm{Ce}} = 2\frac{6.86\ \mathrm{g}}{568.424\ \mathrm{g\,mol^{-1}}}\frac{18.8}{200} = 2.26887\times10^{-3}\ \mathrm{mol}.$$

Consequently,

$$\frac{n_{\mathrm{Ce}}}{n_F} = 1.996 \approx 2.$$

Two cerium(III) ions therefore react per hexafluorosilicate ion. The binary precipitate is **cerium(III) fluoride**, $\mathrm{CeF_3}$, containing the six fluorine atoms as two formula units of precipitate.

The net ionic equation is

$$\mathrm{SiF_6}^{2-} + 2\,\mathrm{Ce^{3+}} + 4\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{CeF_3(s)} + \mathrm{Si(OH)_4} + 4\,\mathrm{H^+}.$$

Restoring the sodium and sulfate ions gives

$$\boxed{\mathrm{Na_2SiF_6} + \mathrm{Ce_2(SO_4)_3} + 4\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{CeF_3(s)} + \mathrm{Si(OH)_4} + \mathrm{Na_2SO_4} + 2\,\mathrm{H_2SO_4}}.$$

The species used here have the following names and SMILES:

Name	SMILES
Cerium(III) sulfate	`[Ce+3].[Ce+3].[O-]S(=O)(=O)[O-].[O-]S(=O)(=O)[O-].[O-]S(=O)(=O)[O-]`
Cerium(III) fluoride	`[Ce+3].[F-].[F-].[F-]`
Orthosilicic acid	`O[Si](O)(O)O`
Sodium sulfate	`[Na+].[Na+].[O-]S(=O)(=O)[O-]`
Sulfuric acid	`OS(=O)(=O)O`
Water	`O`
Hexafluorosilicate(2−) ion	`F[Si-2](F)(F)(F)(F)F`
Cerium(III) ion	`[Ce+3]`
Hydrogen ion, or proton	`[H+]`

The disconnected salt SMILES express composition and charges rather than crystal structures. The hexafluorosilicate ion has octahedral coordination, which these SMILES do not explicitly encode.

5.6 — Sodium chloride produced and starting sodium hexafluorosilicate

From its stated preparation, the formula-unit concentration of **G** is

$$c_G = \frac{6.86/568.424}{0.200} = 0.0603423\ \mathrm{mol\,L^{-1}}.$$

The balanced titration equation establishes a 1:1 molar ratio between $\mathrm{Ce_2(SO_4)_3}$ and $\mathrm{Na_2SiF_6}$.

The hydrolysis species are **silicon tetrafluoride**, `F[Si](F)(F)F`, and **hexafluorosilicic acid**, formally represented in ionic form by `[H+].[H+].F[Si-2](F)(F)(F)(F)F`. Silicon dioxide is an extended network solid and has no discrete molecular SMILES.

For the entire solution **J**,

$$n_J(\mathrm{Na_2SiF_6}) = c_G(0.0616\ \mathrm{L}) = 3.71708\times10^{-3}\ \mathrm{mol}.$$

From the given hydrolysis equation,

$$3\,\mathrm{SiF_4} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{SiO_2} + 2\,\mathrm{H_2SiF_6},$$

the 10 mL aliquot of **H** originally contained

$$n_{10\ \mathrm{mL}}\ (\mathrm{SiF_4}) = \frac{3}{2}n_J = 5.57563\times10^{-3}\ \mathrm{mol}.$$

Therefore the complete 1.00 L solution contained

$$n_{\mathrm{total}}\ (\mathrm{SiF_4}) = 5.57563\times10^{-3}\frac{1000}{10} = 0.557563\ \mathrm{mol}.$$

Every consumed formula unit of $\mathrm{Na_2SiF_6}$ supplies one silicon atom to $\mathrm{SiF_4}$. Thus,

$$n_{\mathrm{reacted}}(\mathrm{Na_2SiF_6}) = 0.557563\ \mathrm{mol}.$$

Its two sodium atoms appear in the sodium chloride removed by filtration:

$$n(\mathrm{NaCl}) = 2(0.557563) = 1.11513\ \mathrm{mol}.$$

Using $M(\mathrm{NaCl}) = 58.44\ \mathrm{g\,mol^{-1}}$,

$$\boxed{m(\mathrm{NaCl}) = 1.11513(58.44) = 65.2\ \mathrm{g}}.$$

The 100 mL aliquot of **K** contains

$$n_{\text{100 mL}}\quad (\mathrm{Na_2SiF_6}) = c_G(0.0444\ \mathrm{L}) = 2.67920 \times 10^{-3}\ \mathrm{mol}.$$

Since **K** has a total volume of 10.0 L,

$$n_{\text{unreacted}}(\mathrm{Na_2SiF_6}) = 2.67920 \times 10^{-3}\frac{10.0}{0.100} = 0.267920\ \mathrm{mol}.$$

The initial amount was the sum of reacted and unreacted material:

$$n_{\text{initial}} = 0.557563 + 0.267920 = 0.825482\ \mathrm{mol}.$$

Hence,

$$\boxed{x = 0.825482(188.053) = 155.234\ \mathrm{g} \approx 155\ \mathrm{g}}.$$

5.7 — Mass of chlorotrifluoromethane

The starting reagent is **tetrachloromethane**, `ClC(Cl)(Cl)Cl`.

Dividing each NMR integral by the number of fluorine atoms per molecule gives the molecular mole ratios:

Product	Name and SMILES	Relative amount
$\mathrm{CFCl_3}$	Trichlorofluoromethane, `FC(Cl)(Cl)Cl`	$45.0/1 = 45.0$
$\mathrm{CF_2Cl_2}$	Dichlorodifluoromethane, `FC(F)(Cl)Cl`	$65.0/2 = 32.5$
$\mathrm{CF_3Cl}$	Chlorotrifluoromethane, `FC(F)(F)Cl`	$18.0/3 = 6.0$
$\mathrm{CF_4}$	Tetrafluoromethane, `FC(F)(F)F`	$2.0/4 = 0.5$

Thus, the mole fraction of chlorotrifluoromethane among the fluorinated carbon products is

$$y(\mathrm{CF_3Cl}) = \frac{6.0}{45.0 + 32.5 + 6.0 + 0.5} = \frac{1}{14}.$$

The mass of starting tetrachloromethane that reacted was

$$m_{\text{reacted}}(\mathrm{CCl_4}) = 500.0(1 - 0.778) = 111.0\ \mathrm{g}.$$

Using $M(\mathrm{CCl_4}) = 153.81\ \mathrm{g\,mol^{-1}}$,

$$n_{\text{reacted}}(\mathrm{CCl_4}) = \frac{111.0}{153.81} = 0.721670\ \mathrm{mol}.$$

Each fluorinated carbon product contains one carbon atom, so their combined amount equals the amount of tetrachloromethane consumed:

$$n(\mathrm{CF_3Cl}) = \frac{0.721670}{14} = 0.0515478\ \mathrm{mol}.$$

With $M(\mathrm{CF_3Cl}) = 104.46\ \mathrm{g\,mol^{-1}}$,

$$\boxed{m(\mathrm{CF_3Cl}) = 0.0515478(104.46) = 5.38\ \mathrm{g}}.$$

The solution was checked against the official solution.

Problem 6: The Solid-State Chemistry of Transition Metals



Volcano at Sakurajima island

PART A

Japan is one of the countries with the highest numbers of volcanos worldwide. When silicate minerals crystallize from magma, a part of the transition-metal ions (M^{n+}) in the magma is incorporated into the silicate minerals. The M^{n+} studied in the problem are coordinated by oxide ions (O^{2-}) and adopt a four-coordinate tetrahedral (T_d) geometry in the magma and six-coordinate octahedral (O_h) geometry in the silicate minerals, both of which exhibit a high-spin electron configuration. The distribution coefficient of M^{n+} between the silicate minerals and magma, D, can be expressed by:

$$D = \frac{[\mathrm{M}]_\mathrm{s}}{[\mathrm{M}]_\mathrm{l}}$$

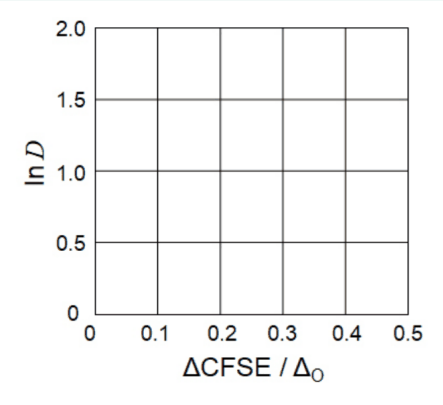
where $[\mathrm{M}]_\mathrm{s}$ and $[\mathrm{M}]_\mathrm{l}$ are the concentrations of M^{n+} in the silicate minerals and the magma, respectively. The table below shows the D values of Cr^{2+} and Mn^{2+} as examples.

	Cr^{2+}	Mn^{2+}
D	7.2	1.1

Let Δ_O and CFSE^O be the energy separation of the d-orbitals of M^{n+} and the crystal-field stabilization energy in a O_h field, respectively. Let Δ_T and CFSE^T be those in a T_d field.

6.1 Calculate $\left|\mathrm{CFSE}^\mathrm{O} - \mathrm{CFSE}^\mathrm{T}\right| = \Delta\mathrm{CFSE}$ in terms of Δ_O for Cr^{2+}, Mn^{2+}, and Co^{2+}; assume $\Delta_\mathrm{T} = 4/9\Delta_\mathrm{O}$.

6.2 A linear relationship is observed by plotting $\ln D$ against $\Delta\mathrm{CFSE}/\Delta_\mathrm{O}$ in the Cartesian coordinate system shown below. Estimate D for Co^{2+}.



Metal oxides MO (M: Ca, Ti, V, Mn, or Co) crystallize in a rock-salt structure wherein the M^{n+} adopts an O_h geometry with a high-spin electron configuration. The lattice enthalpy of these oxides is mainly governed by the Coulomb interactions based on the radius and charge of the ions and some contributions from the CFSE of M^{n+} in the O_h field.

6.3 Choose the appropriate set of lattice enthalpies [$\mathrm{kJ\,mol^{-1}}$] from one of the options (a) to (f).

	CaO	TiO	VO	MnO	CoO
(a)	3460	3878	3913	3810	3916
(b)	3460	3916	3878	3810	3913
(c)	3460	3913	3916	3810	3878
(d)	3810	3878	3913	3460	3916
(e)	3810	3916	3878	3460	3913
(f)	3810	3913	3916	3460	3878

PART B

A mixed oxide **A**, which contains La^{3+} and Cu^{2+}, crystallizes in a tetragonal unit cell shown in Fig.1. In the $[\mathrm{CuO_6}]$ octahedron, the Cu–O length along the z-axis (l_z) is longer than that of the x-axis (l_x), and $[\mathrm{CuO_6}]$ is distorted from the regular O_h geometry. This distortion removes the degeneracy of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}).

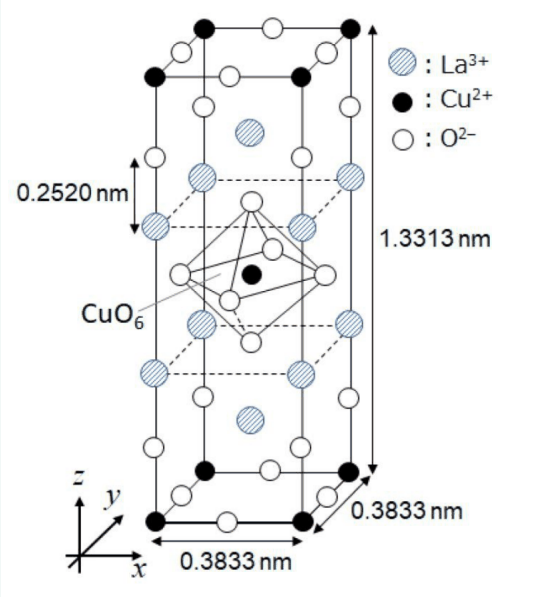


Fig. 1

A can be synthesized by thermal decomposition (pyrolysis) of complex **B**, which is formed by mixing metal chlorides in dilute aqueous ammonia solution containing squaric acid $\mathrm{C_4H_2O_4}$, i.e., a diacid. The pyrolysis behavior of **B** in dry air shows a weight loss of 29.1% up to $200\ ^\circ\mathrm{C}$ due to the loss of crystallization water, followed by another weight loss up to $700\ ^\circ\mathrm{C}$ due to the release of $\mathrm{CO_2}$. The total weight loss during the formation of **A** from **B** is 63.6%. It should be noted that only water and $\mathrm{CO_2}$ are released in the pyrolysis reaction.

6.4 Write the chemical formulae for **A** and **B**.

6.5 Calculate l_x and l_z using Fig. 1.

6.6 For $\mathrm{Cu^{2+}}$ in the distorted $[\mathrm{CuO_6}]$ octahedron in **A** of Fig. 1, write the names of the split e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) in (i) and (ii), and draw the electron configuration in the dotted box in your answer sheet.

A is an insulator. When one $\mathrm{La^{3+}}$ is substituted with one $\mathrm{Sr^{2+}}$, one hole is generated in the crystal lattice that can conduct electricity. As a result, the $\mathrm{Sr^{2+}}$-doped **A** shows superconductivity below 38 K. When a substitution reaction took place for **A**, 2.05×10^{27} holes $\mathrm{m^{-3}}$ were generated.

6.7 Calculate the percentage of $\mathrm{Sr^{2+}}$ substituted for $\mathrm{La^{3+}}$ based on the mole ratio in the substitution reaction. Note that the valences of the constituent ions and the crystal structure are not altered by the substitution reaction

PART C

$\mathrm{Cu_2(CH_3CO_2)_4}$ is composed of four $\mathrm{CH_3CO_2^-}$ coordinated to two $\mathrm{Cu^{2+}}$ (Fig. 2A). $\mathrm{Cu_2(CH_3CO_2)_4}$ exhibits high levels of structural symmetry, with two axes passing through the carbon atoms of the four $\mathrm{CH_3CO_2^-}$ and an axis passing through the two $\mathrm{Cu^{2+}}$, all of which are oriented orthogonal relative to each other. When a dicarboxylate ligand is used instead of $\mathrm{CH_3CO_2^-}$, a "cage complex" is formed. The cage complex $\mathrm{Cu_4(L_1)_4}$ is composed of planar dicarboxylate **L1** (Fig. 2B) and $\mathrm{Cu^{2+}}$ (Fig. 2C). The angle θ between the coordination directions of the two carboxylates, indicated by the arrows in Fig. 2B, determines the structure of the cage complex. The θ is 0° for **L1**. Note that hydrogen atoms are not shown in Fig. 2.

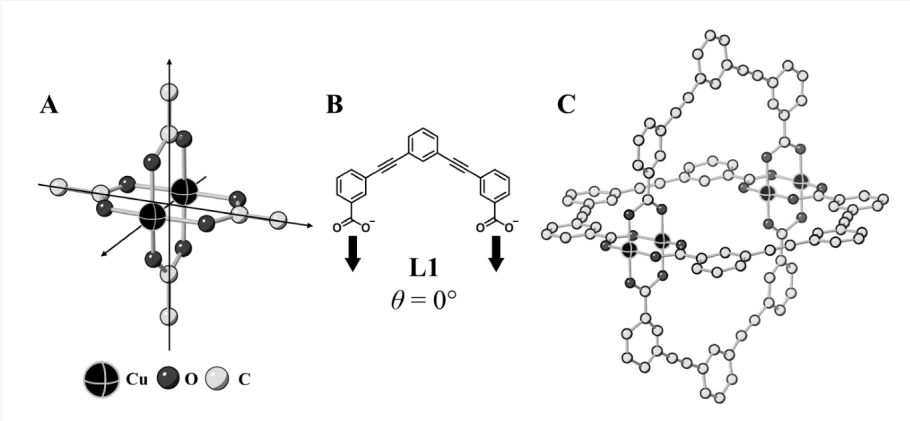
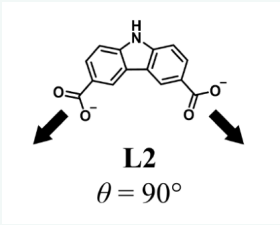


Fig. 2

6.8 The θ of the planar dicarboxylate **L2** below is fixed to 90°. If the composition of the cage complex formed from **L2** and $\mathrm{Cu^{2+}}$ is $\mathrm{Cu_n(L_2)_m}$, give the smallest integer combination of n and m. Assume that only the $\mathrm{CO_2^-}$ groups of **L2** form a coordination bond to $\mathrm{Cu^{2+}}$ ions.



A zinc complex, $\mathrm{Zn_4O(CH_3CO_2)_6}$, contains four tetrahedral $\mathrm{Zn^{2+}}$, six $\mathrm{CH_3CO_2^-}$, and one $\mathrm{O^{2-}}$ (Fig. 3A). In $\mathrm{Zn_4O(CH_3CO_2)_6}$, the $\mathrm{O^{2-}}$ is located at the origin, and the three axes passing through the carbon atoms of $\mathrm{CH_3CO_2^-}$ are oriented orthogonal relative to each other. When p-benzenedicarboxylate (Fig. 3B, **L3**, $\theta = 180^\circ$) is used instead of $\mathrm{CH_3CO_2^-}$, the $\mathrm{Zn^{2+}}$ clusters are linked to each other to form a crystalline solid (**X**) that is called a "porous coordination polymer" (Fig. 3C). The composition of **X** is $[\mathrm{Zn_4O(L_3)_3}]_n$, and it has a cubic crystal structure with nano-sized pores. One pore is represented as a sphere in Fig. 3D, and each tetrahedral $\mathrm{Zn^{2+}}$ cluster is represented as a dark gray polyhedron in Fig. 3C and 3D. Note that hydrogen atoms are not shown in Fig. 3.

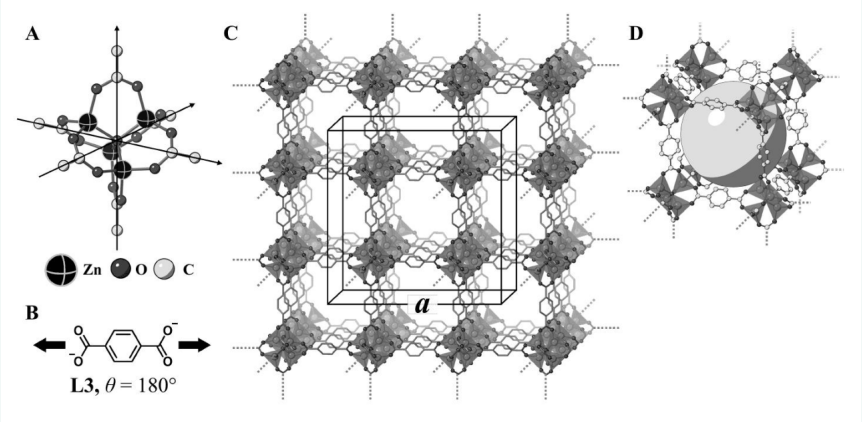


Fig. 3

6.9 X has a cubic unit cell with a side length of a (Fig. 3C) and a density of $0.592\,\mathrm{g\,cm^{-3}}$. Calculate a in [cm].

6.10 X contains a considerable number of pores, and 1 g of **X** can accommodate 3.0×10^2 mL of $\mathrm{CO_2}$ gas in the pores at 1 bar and $25\,^{\circ}\mathrm{C}$. Calculate the average number of $\mathrm{CO_2}$ molecules per pore.

Official English text of the problem.

Answers

- **6.1:** $\mathrm{Cr^{2+}}$: $\dfrac{19}{45}\Delta_{\mathrm{O}}$; $\mathrm{Mn^{2+}}$: 0; $\mathrm{Co^{2+}}$: $\dfrac{4}{15}\Delta_{\mathrm{O}}$.
- **6.2:** $D(\mathrm{Co^{2+}}) \approx \boxed{3.6}$.
- **6.3: Option (a)**: $3460,\ 3878,\ 3913,\ 3810,\ 3916\,\mathrm{kJ\,mol^{-1}}$, respectively.
- **6.4:** $\boxed{\mathbf{A} = \mathrm{La_2CuO_4}}$; $\boxed{\mathbf{B} = \mathrm{La_2Cu(C_4O_4)_4 \cdot 18\,H_2O}}$.
- **6.5:** $\boxed{l_x = 0.1917\,\mathrm{nm}, \quad l_z = 0.2068\,\mathrm{nm}}$.
- **6.6:** Higher e_g level: $d_{x^2-y^2}$, one electron; lower e_g level: d_{z^2}, two electrons. The three t_{2g}-derived orbitals are all doubly occupied.
- **6.7:** $\boxed{10.0\%}$ of the original La sites are substituted; approximately $\mathrm{La_1 \cdot 80\,Sr_0 \cdot 20\,CuO_4}$.
- **6.8:** $\boxed{n = m = 12}$, giving $\mathrm{Cu_{12}(L_2)_{12}}$.
- **6.9:** $\boxed{a = 2.59 \times 10^{-7}\,\mathrm{cm}}$.
- **6.10:** $\boxed{9.3\text{ molecules of }\mathrm{CO_2}\text{ per pore}}$, on average.

Solution

For the extended solids and coordination assemblies, the SMILES below identify their constituent ions and ligands. Their spatial arrangements and connections are described separately; component SMILES do not encode the periodic lattice or cage geometry.

6.1 — Crystal-field stabilization energies

The metal ions are chromium(II), $\mathrm{Cr^{2+}}$, `[Cr+2]`; manganese(II), $\mathrm{Mn^{2+}}$, `[Mn+2]`; and cobalt(II), $\mathrm{Co^{2+}}$, `[Co+2]`. Their configurations are d^4, d^5, and d^7, respectively.

Taking the orbital barycentre as zero, the octahedral orbital energies are

$$E(t_{2g}) = -\frac{2}{5}\Delta_{\mathrm{O}}, \qquad E(e_g) = +\frac{3}{5}\Delta_{\mathrm{O}},$$

whereas the tetrahedral orbital energies are

$$E(e) = -\frac{3}{5}\Delta_{\mathrm{T}}, \qquad E(t_2) = +\frac{2}{5}\Delta_{\mathrm{T}}.$$

Filling all orbitals according to the specified high-spin configurations gives:

Ion	Octahedral configuration	$\mathrm{CFSE^O}$	Tetrahedral configuration	$\mathrm{CFSE^T}$
$\mathrm{Cr^{2+}}$, d^4	$t_{2g}^3 e_g^1$	$-\frac{3}{5}\Delta_{\mathrm{O}}$	$e^2 t_2^2$	$-\frac{2}{5}\Delta_{\mathrm{T}}$
$\mathrm{Mn^{2+}}$, d^5	$t_{2g}^3 e_g^2$	0	$e^2 t_2^3$	0
$\mathrm{Co^{2+}}$, d^7	$t_{2g}^5 e_g^2$	$-\frac{4}{5}\Delta_{\mathrm{O}}$	$e^4 t_2^3$	$-\frac{6}{5}\Delta_{\mathrm{T}}$

Using $\Delta_{\mathrm{T}} = \frac{4}{9}\Delta_{\mathrm{O}}$,

$$\Delta\mathrm{CFSE}(\mathrm{Cr^{2+}}) = \left|-\frac{3}{5} + \frac{2}{5}\frac{4}{9}\right|\Delta_{\mathrm{O}} = \boxed{\frac{19}{45}\Delta_{\mathrm{O}}},$$

$$\Delta\mathrm{CFSE}(\mathrm{Mn^{2+}}) = \boxed{0},$$

$$\Delta\mathrm{CFSE}(\mathrm{Co^{2+}}) = \left|-\frac{4}{5} + \frac{6}{5}\frac{4}{9}\right|\Delta_{\mathrm{O}} = \boxed{\frac{4}{15}\Delta_{\mathrm{O}}}.$$

The numbers of paired electrons are unchanged between the two geometries for each ion, so a pairing-energy term would cancel in these differences.

6.2 — Distribution coefficient of cobalt(II)

Set

$$x = \frac{\Delta\mathrm{CFSE}}{\Delta_\mathrm{O}}, \qquad y = \ln D.$$

The two known points are

$$\mathrm{Mn}^{2+}: \ (0, \ln 1.1) = (0, 0.09531),$$
$$\mathrm{Cr}^{2+}: \ \left(\frac{19}{45}, \ln 7.2\right) = (0.42222, 1.97408).$$

Thus the straight line to draw on the supplied axes is

$$y = 0.09531 + 4.44972x.$$

For cobalt(II), $x = 4/15$, so

$$\begin{aligned}\ln D_{\mathrm{Co}^{2+}} &= \ln 1.1 + \frac{4/15}{19/45}(\ln 7.2 - \ln 1.1)\\ &= \ln 1.1 + \frac{12}{19}\ln\left(\frac{7.2}{1.1}\right)\\ &= 1.28190.\end{aligned}$$

Therefore,

$$\boxed{D_{\mathrm{Co}^{2+}} = e^{1.28190} = 3.6035 \approx 3.6}.$$

On the graph, mark the cobalt point at approximately $(0.267, 1.282)$.

6.3 — Lattice enthalpies

All five oxides contain divalent metal ions and oxide ions, O^{2-}, `[O-2]`. Their relevant electronic configurations are:

Oxide and name	Ionic-component SMILES	Metal configuration	Octahedral CFSE
CaO, calcium oxide	`[Ca+2].[O-2]`	d^0	0
TiO, titanium(II) oxide	`[Ti+2].[O-2]`	d^2	$-0.8\Delta_\mathrm{O}$
VO, vanadium(II) oxide	`[V+2].[O-2]`	d^3	$-1.2\Delta_\mathrm{O}$
MnO, manganese(II) oxide	`[Mn+2].[O-2]`	High-spin d^5	0
CoO, cobalt(II) oxide	`[Co+2].[O-2]`	High-spin d^7	$-0.8\Delta_\mathrm{O}$

The lattices are extended rock-salt structures, with each metal surrounded octahedrally by six oxide ions.

Neither calcium(II) nor high-spin manganese(II) has CFSE. The smaller manganese(II) ion gives stronger Coulomb attraction, so

$$U(\mathrm{CaO}) < U(\mathrm{MnO}).$$

This eliminates options (d)–(f).

Titanium(II) and cobalt(II) have the same CFSE coefficient, while the later, smaller cobalt(II) ion gives stronger electrostatic binding. Thus

$$U(\mathrm{CoO}) > U(\mathrm{TiO}),$$

which selects **(a)** among the remaining choices. The stronger CFSE of d^3 vanadium(II) also supports VO lying above TiO.

The positive lattice-enthalpy values in the question are therefore

	CaO	TiO	VO	MnO	CoO
$U/(\mathrm{kJ\,mol^{-1}})$	3460	3878	3913	3810	3916

6.4 — Formulae of A and B

First count the ions in the unit cell, accounting for sharing with neighbouring cells.

Species	Count in Fig. 1	Number per unit cell
Cu^{2+}	Eight corners and one interior site	$8(\frac{1}{8}) + 1 = 2$
La^{3+}	Eight edge sites and two interior sites	$8(\frac{1}{4}) + 2 = 4$
O^{2-}	Sixteen edge sites, four face sites, and two interior sites	$16(\frac{1}{4}) + 4(\frac{1}{2}) + 2 = 8$

The unit-cell composition is therefore $\mathrm{La_4Cu_2O_8}$, giving

$$\boxed{\mathbf{A} = \mathrm{La_2CuO_4}}.$$

This is **lanthanum(III) copper(II) oxide**, also called lanthanum cuprate. Its constituent ions are lanthanum(III), `[La+3]`; copper(II), `[Cu+2]`; and oxide, `[O-2]`. A composition-only ionic SMILES is `[La+3].[La+3].[Cu+2].[O-2].[O-2].[O-2].[O-2]`.

Squaric acid, $\mathrm{C_4H_2O_4}$, has SMILES `O=C1C(=O)C(O)=C1O`. Its doubly deprotonated ligand is the **squarate dianion**, $\mathrm{C_4O_4}^{2-}$, `O=C1C(=O)C([O-])=C1[O-]`; this SMILES shows one resonance form.

The total metal charge per $\mathrm{La_2Cu}$ unit is

$$2(+3) + (+2) = +8,$$

requiring four squarate dianions. Hence write

$$\mathbf{B} = \mathrm{La_2Cu(C_4O_4)_4 \cdot \mathit{x}H_2O}.$$

Using conventional atomic masses,

$$M_A = 2(138.91) + 63.55 + 4(16.00) = 405.37\,\mathrm{g\,mol^{-1}}.$$

Since the final residue is $100 - 63.6 = 36.4\%$ of the initial mass,

$$M_B = \frac{405.37}{0.364} = 1113.65\,\mathrm{g\,mol^{-1}}.$$

Crystallization water accounts for 29.1% of this mass:

$$x = \frac{0.291(1113.65)}{18.016} = 17.99 \approx 18.$$

Thus

$$\boxed{\mathbf{B} = \mathrm{La_2Cu(C_4O_4)_4 \cdot 18\,H_2O}},$$

lanthanum(III) copper(II) squarate octadecahydrate. Its components are two `[La+3]` ions, one `[Cu+2]` ion, four squarate dianions with the SMILES above, and eighteen water molecules, `O`. The empirical formula does not determine all metal–ligand connections in B.

The balanced overall pyrolysis in air is

$$\boxed{\mathrm{La_2Cu(C_4O_4)_4 \cdot 18\,H_2O + 10\,O_2 \longrightarrow La_2CuO_4 + 16\,CO_2 + 18\,H_2O}}.$$

Here dioxygen is `O=O`, carbon dioxide is `O=C=O`, and water is `O`.

Oxygen uptake is necessary: the net mass loss during oxidation is the mass of escaping carbon dioxide minus the mass of oxygen absorbed. With $M_B = 1113.818\,\mathrm{g\,mol^{-1}}$, the predicted losses are

$$\frac{18(18.016)}{1113.818} \times 100 = 29.115\%,$$

and

$$\left(1 - \frac{405.37}{1113.818}\right) \times 100 = 63.605\%,$$

both matching the supplied values.

6.5 — Copper–oxygen distances

Along x, oxygen lies halfway between neighbouring copper sites:

$$l_x = \frac{0.3833}{2} = \boxed{0.1917\,\mathrm{nm}}.$$

Along z, adjacent copper planes are separated by $c/2$. The marked $0.2520\,\mathrm{nm}$ interval lies between their facing apical-oxygen planes, giving

$$l_z + 0.2520 + l_z = \frac{1.3313}{2}.$$

Therefore,

$$l_z = \frac{1.3313/2 - 0.2520}{2} = 0.206825\,\mathrm{nm} \approx \boxed{0.2068\,\mathrm{nm}}.$$

As specified in the problem, $l_z > l_x$.

6.6 — Splitting and electron configuration

Copper(II) is d^9. Elongation along z weakens the interaction between the axial oxide ligands and d_{z^2}, lowering this orbital relative to $d_{x^2-y^2}$.

Thus, within the split e_g pair,

$$\boxed{E(d_{x^2-y^2}) > E(d_{z^2})}.$$

The required drawing has:

Level	Orbital	Electrons
Higher split e_g level	$d_{x^2-y^2}$	$\uparrow$
Lower split e_g level	d_{z^2}	$\uparrow\downarrow$
Three t_{2g}-derived orbitals	d_{xy}, d_{xz}, d_{yz}	$\uparrow\downarrow$ in each

In words, draw two separated horizontal e_g lines, put one electron on the upper $d_{x^2-y^2}$ line and a pair on the lower d_{z^2} line. The other six d electrons form three pairs.

If answer-sheet label (i) denotes the upper line and (ii) the lower line, then

$$\text{(i)} = d_{x^2-y^2}, \qquad \text{(ii)} = d_{z^2}.$$

6.7 — Percentage substitution by strontium

The unit-cell volume is

$$\begin{aligned} V_{\mathrm{cell}} &= (0.3833\,\mathrm{nm})^2(1.3313\,\mathrm{nm}) \\ &= 0.1955931\,\mathrm{nm}^3 \\ &= 1.955931 \times 10^{-28}\,\mathrm{m}^3. \end{aligned}$$

The number of holes per cell is

$$N_h = (2.05 \times 10^{27}\,\mathrm{m^{-3}})(1.955931 \times 10^{-28}\,\mathrm{m}^3) = 0.400966.$$

Each strontium(II) ion, $\mathrm{Sr^{2+}}$, `[Sr+2]`, produces one hole, so this also equals the average number of substituted La sites per cell.

There are four La sites per undoped cell. Consequently,

$$\boxed{\text{substitution percentage} = \frac{0.400966}{4} \times 100 = 10.0\%.}$$

There are two formula units per cell, so the Sr content per formula unit is

$$x = \frac{0.400966}{2} = 0.20048.$$

The approximate composition is therefore

$$\mathrm{La_{2-x}Sr_xCuO_4} \approx \mathrm{La_1 \cdot 80\,Sr_0 \cdot 20\,CuO_4}.$$

The holes provide the specified charge compensation without assigning a changed formal valence to the constituent ions.

6.8 — Smallest cage formed by L2

The reference acetate ligand is **acetate (ethanoate)**, $\mathrm{CH_3CO_2^-}$, `CC(=O)[O-]`.

L2 is **9H-carbazole-3,6-dicarboxylate**, with SMILES `O=C([O-])c1ccc2[nH]c3ccc(C(=O)[O-])cc3c2c1`. Its two carboxylates coordinate; the N–H group remains uncoordinated. The imposed planar conformation and 90° angle are geometric information not fixed by the SMILES alone.

Each copper-carboxylate paddlewheel contains two copper ions and has four carboxylate connection directions arranged as a square around its Cu–Cu axis.

With a 90° linker, the smallest closed assembly places **six paddlewheel units at the vertices of an octahedron**. Equivalently, put their centres on the $+x, -x, +y, -y, +z, -z$ directions. Each vertex connects to its four adjacent vertices, and opposite vertices are unconnected.

Therefore:

$$n = 6 \times 2 = 12$$

copper ions, and

$$m = \frac{6 \times 4}{2} = 12$$

dicarboxylate ligands, because each ligand connects two paddlewheels.

Hence

$$\boxed{n = m = 12, \qquad \mathrm{Cu_{12}(L_2)_{12}}}.$$

These are the counts in a complete cage. Charge balance alone establishes only $n = m$.

6.9 — Cubic unit-cell edge

L3 is **terephthalate (benzene-1,4-dicarboxylate)**, $\mathrm{C_8H_4O_4^{2-}}$, with SMILES `O=C([O-])c1ccc(C(=O)[O-])cc1`.

The metal building block contains four zinc(II) ions, `[Zn+2]`, arranged tetrahedrally about a central oxide ion, `[O-2]`. Its six linker connections extend along three mutually perpendicular axes. The resulting solid is a zinc(II) oxide–terephthalate coordination polymer.

Figure 3C shows **two cluster spacings along each unit-cell edge**, so the depicted cell contains

$$Z = 2^3 = 8$$

$\mathrm{Zn_4O(L_3)_3}$ formula units.

The formula-unit molar mass is

$$\begin{aligned} M &= 4(65.38) + 16.00 + 3\,[8(12.01) + 4(1.008) + 4(16.00)] \\ &= 769.856\,\mathrm{g\,mol^{-1}}. \end{aligned}$$

Using $N_\mathrm{A} = 6.02214076 \times 10^{23}\,\mathrm{mol^{-1}}$,

$$\rho = \frac{ZM}{N_\mathrm{A} a^3},$$

and therefore

$$\begin{aligned} a &= \left(\frac{8(769.856)}{(6.02214076 \times 10^{23})(0.592)} \right)^{1/3} \mathrm{cm} \\ &= 2.58509 \times 10^{-7}\,\mathrm{cm}. \end{aligned}$$

Thus

$$\boxed{a = 2.59 \times 10^{-7}\,\mathrm{cm}}$$

or approximately $2.59\,\mathrm{nm}$.

6.10 — Average number of carbon dioxide molecules per pore

Each elementary cubic pore is bounded by eight cluster nodes, while each node belongs to eight neighbouring pores. Thus the numbers of pores and cluster nodes are equal: **eight pores per depicted unit cell**, or one pore per $\mathrm{Zn_4O(L_3)_3}$ formula unit.

For $1.00\,\mathrm{g}$ of X,

$$N_\mathrm{pores} = \frac{1.00\,\mathrm{g}}{769.856\,\mathrm{g\,mol^{-1}}} N_\mathrm{A} = 7.8224 \times 10^{20}.$$

The supplied gas volume is

$$V = 3.0 \times 10^2\,\mathrm{mL} = 0.300\,\mathrm{L}, \qquad T = 298.15\,\mathrm{K}.$$

Using the ideal-gas equation with $R = 0.08314\,\mathrm{L\,bar\,mol^{-1}\,K^{-1}}$,

$$n_{\mathrm{CO_2}} = \frac{PV}{RT} = \frac{(1\,\mathrm{bar})(0.300\,\mathrm{L})}{(0.08314\,\mathrm{L\,bar\,mol^{-1}\,K^{-1}})(298.15\,\mathrm{K})} = 0.0121025\,\mathrm{mol}.$$

The average occupancy is consequently

$$\begin{aligned}\frac{N_{\mathrm{CO_2}}}{N_{\mathrm{pores}}} &= \frac{0.0121025\,N_{\mathrm{A}}}{(1.00/769.856)N_{\mathrm{A}}} \\ &= 9.3172.\end{aligned}$$

To the precision of the gas-volume data,

$$\boxed{9.3 \text{ carbon dioxide molecules per pore, on average.}}$$

The solution was checked against the official solution.

Problem 7: Playing with Non-benzenoid Aromaticity

Prof. Nozoe (1902–1996) opened the research field of non-benzenoid aromatic compounds, which are now ubiquitous in organic chemistry.



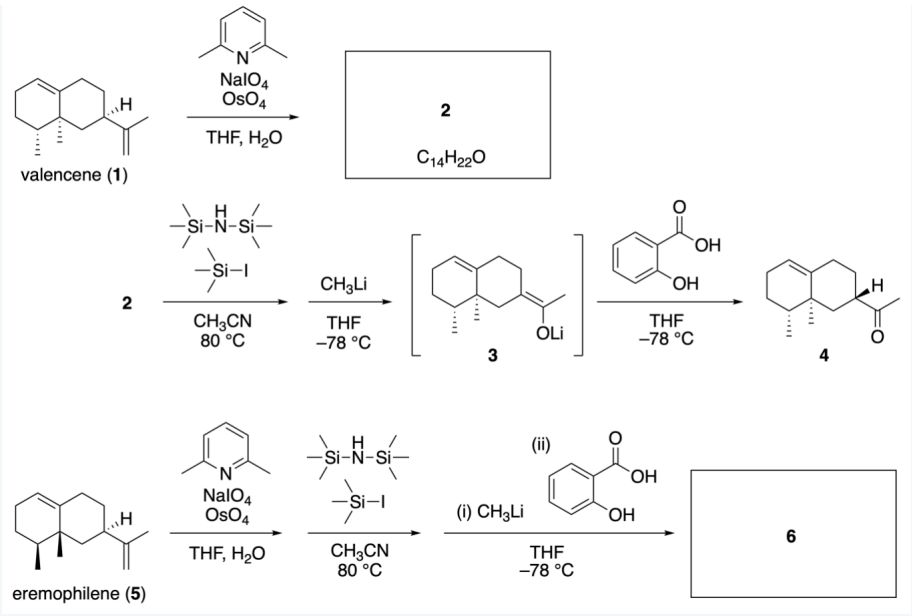
Photo courtesy: Tohoku Univ.

PART A

Lineariifolianone is a natural product with a unique structure, which was isolated from *Inula linariifolia*. From valencene (**1**), a one-step conversion yields **2**, before a three-step conversion via **3** yields ketone **4**. Eremophilene (**5**) is converted into **6** by performing the same four-step conversion.

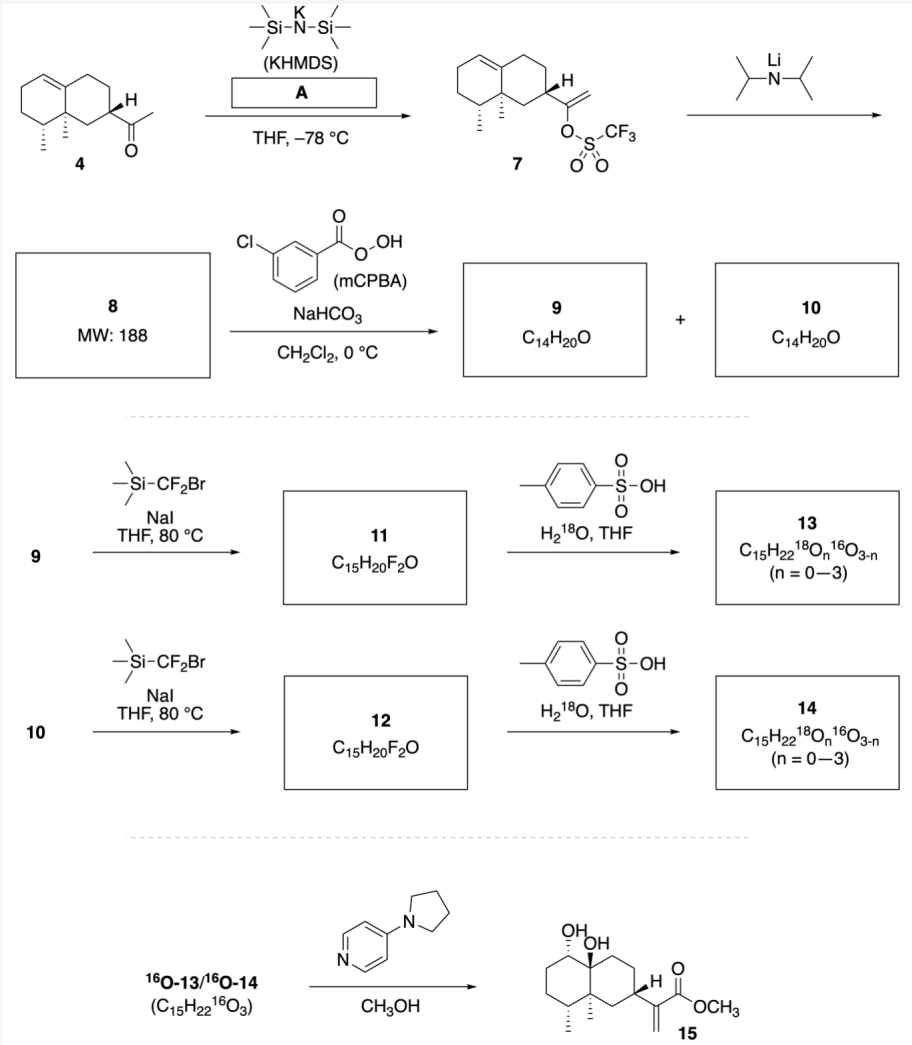


Inula linariifolia

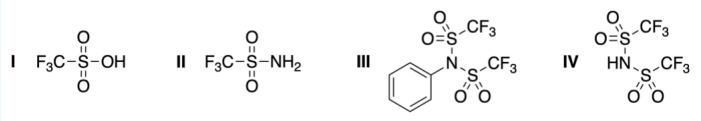


7.1 Draw the structures of **2** and **6** and clearly identify the stereochemistry where necessary.

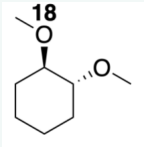
Then, ketone **4** is converted into ester **15**. Compound **8** (molecular weight: 188) retains all the stereocenters in **7**. Compounds **9** and **10** have five stereocenters and no carbon-carbon double bonds. Assume that $\mathrm{H_2}\,^{18}\mathrm{O}$ is used instead of $\mathrm{H_2}\,^{16}\mathrm{O}$ for the synthesis of $^{18}\mathrm{O}$-labelled-linearifolianones **13** and **14** from **11** and **12**, respectively. Compounds **13** and **14** are $^{18}\mathrm{O}$-labelled isotopomers. Ignoring isotopic labelling, both **13** and **14** provide the same product **15** with identical stereochemistry.



7.2 Choose the appropriate structure for **A**.

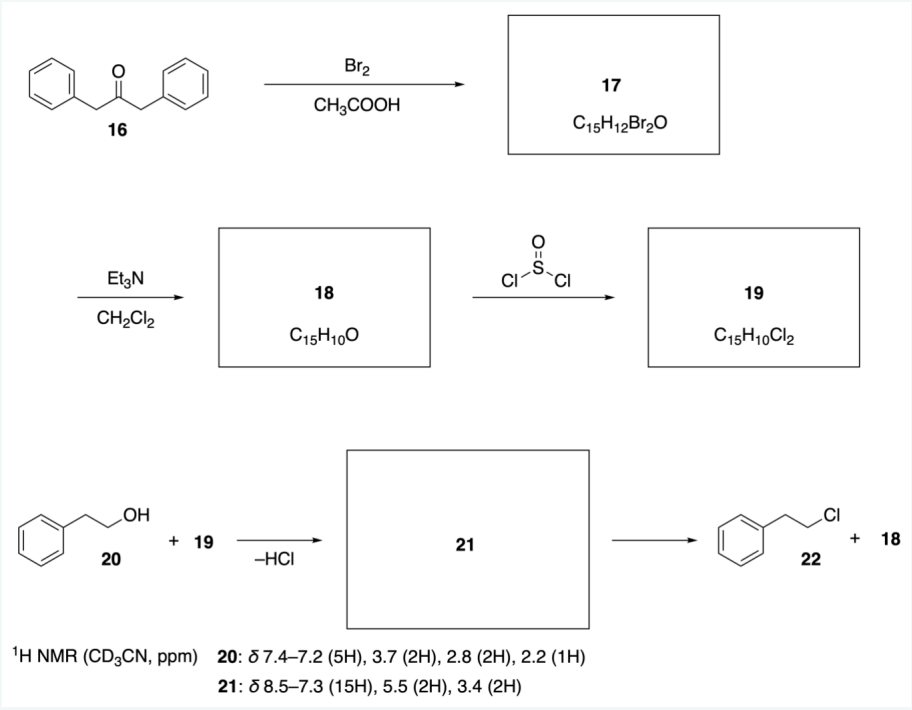


7.3 Draw the structures of **8–14** and clearly identify the stereochemistry where necessary. Also, indicate the introduced ^{18}O atoms for **13** and **14** as shown in the example below.



PART B

Compound **19** is synthesized as shown below. In relation to non-benzenoid aromaticity, **19** can be used as an activator for alcohols, and **20** was converted to **22** via ion-pair intermediate **21**. Although the formation of **21** was observed by NMR, **21** gradually decomposes to give **18** and **22**.



7.4 Draw the structures of **17–19** and **21**. Identifying the stereochemistry is not necessary.

Official English text of the problem.

Answers

For the Part A names and descriptions, number the bicyclo[4.4.0]decane skeleton as follows: **C1 is the upper ring junction**, and C1–C2–C3–C4–C5–C6 runs around the left ring to the lower junction. C6–C7–C8–C9–C10–C1 completes the right ring. The methyl groups are at **C5 and C6**, and the side chain is at **C8**. “Front” means a solid wedge; “back” means a hashed wedge, in the orientation of the supplied drawings.

- **7.1**

2 — 1-[(5R,6S,8R)-5,6-dimethylbicyclo[4.4.0]dec-1-en-8-yl]ethan-1-one.

SMILES: `CC(=O)[C@@H]1CCC2=CCC[C@@H](C)[C@]2(C)C1`

Replace the isopropenyl group of **1** by an acetyl group. Both methyl groups and the explicitly shown C8 hydrogen remain **behind** the paper.

6 — 1-[(5S,6R,8R)-5,6-dimethylbicyclo[4.4.0]dec-1-en-8-yl]ethan-1-one.

SMILES: `CC(=O)[C@@H]1CCC2=CCC[C@H](C)[C@@]2(C)C1`

Both methyl groups point **toward** the viewer, and the C8 hydrogen points **behind** the paper. **6 is the enantiomer of 4.**

- **7.2**

A is III, N-phenylbis(trifluoromethanesulfonyl)amine, commonly called **N-phenyltriflimide**, $\mathrm{PhNTf_2}$.

SMILES: `O=S(=O)(C(F)(F)F)N(c1ccccc1)S(=O)(=O)C(F)(F)F`

- **7.3**

The following consistently assigns **9** to the front-face epoxide. Interchanging **9/10**, **11/12**, and **13/14** together is equivalent.

8 — (5R,6S,8S)-8-ethynyl-5,6-dimethylbicyclo[4.4.0]dec-1-ene.

SMILES: `C#C[C@H]1CCC2=CCC[C@@H](C)[C@]2(C)C1`

9 — (1S,2R,5R,6S,8S)-1,2-epoxy-8-ethynyl-5,6-dimethylbicyclo[4.4.0]decane.

SMILES: `C#C[C@H]1CC[C@@]23O[C@@H]2CC[C@@H](C)[C@]3(C)C1`

The epoxide oxygen is **in front** of the original C1–C2 bond.

10 — (1R,2S,5R,6S,8S)-1,2-epoxy-8-ethynyl-5,6-dimethylbicyclo[4.4.0]decane.

SMILES: `C#C[C@H]1CC[C@]23O[C@H]2CC[C@@H](C)[C@]3(C)C1`

The epoxide oxygen is **behind** the original C1–C2 bond.

11 — (1S,2R,5R,6S,8S)-8-(3,3-difluorocycloprop-1-en-1-yl)-1,2-epoxy-5,6-dimethylbicyclo[4.4.0]decane.

SMILES: `FC1(F)C=C1[C@H]1CC[C@@]23O[C@@H]2CC[C@@H](C)[C@]3(C)C1`

12 — (1R,2S,5R,6S,8S)-8-(3,3-difluorocycloprop-1-en-1-yl)-1,2-epoxy-5,6-dimethylbicyclo[4.4.0]decane.

SMILES: `FC1(F)C=C1[C@H]1CC[C@]23O[C@H]2CC[C@@H](C)[C@]3(C)C1`

13 — Lineariifolianone labelled with $^{18}\mathrm{O}$ at the cyclopropenone carbonyl and the C2 hydroxyl oxygen.

SMILES: `[18O]=C1C=C1[C@H]1CC[C@@]2([16OH])[C@@H]([18OH])CC[C@@H](C)[C@]2(C)C1`

14 — Lineariifolianone labelled with $^{18}\mathrm{O}$ at the cyclopropenone carbonyl and the C1 hydroxyl oxygen.

SMILES: `[18O]=C1C=C1[C@H]1CC[C@@]2([18OH])[C@@H]([16OH])CC[C@@H](C)[C@]2(C)C1`

In both **13** and **14**, C1–OH points **forward**, C2–OH points **backward**, both methyl groups point backward, and C8–H points forward. Both have $n = 2$, with formula $\mathrm{C_{15}H_{22}\,{}^{18}O_2\,{}^{16}O}$.

- **7.4**

Compound	Name	SMILES
17	1,3-Dibromo-1,3-diphenylpropan-2-one	`O=C(C(Br)c1ccccc1)C(Br)c1ccccc1`
18	2,3-Diphenylcycloprop-2-en-1-one, or diphenylcyclopropenone	`O=C1C(c2ccccc2)=C1c1ccccc1`
19	3,3-Dichloro-1,2-diphenylcycloprop-1-ene	`ClC1(Cl)C(c2ccccc2)=C1c1ccccc1`
21	1-(2-Phenylethoxy)-2,3-diphenylcyclopropenium chloride	`[Cl-].[C+]1(OCCc2ccccc2)C(c2ccccc2)=C1c1ccccc1`

In **21**, the positive charge is delocalized around the planar three-membered ring and into the alkoxy substituent. The SMILES shows one resonance contributor.

Solution

7.1 — Oxidative cleavage and stereoselective reprotonation

The starting compounds are valencene **1**, `C=C(C)[C@@H]1CCC2=CCC[C@@H](C)[C@]2(C)C1`, and eremophilene **5**, `C=C(C)[C@@H]1CCC2=CCC[C@H](C)[C@@]2(C)C1`.

The $\mathrm{OsO_4/NaIO_4}$ reaction cleaves the terminal isopropenyl double bond. Its substituted carbon becomes the ketone carbonyl; the terminal methylene carbon gives formaldehyde, `C=O`. The ring double bond remains intact.

The balanced overall oxidation, applicable to either starting hydrocarbon, is

$$\mathrm{C_{15}H_{24} + 2\,NaIO_4 \longrightarrow C_{14}H_{22}O + CH_2O + 2\,NaIO_3}.$$

Consequently, **2** is the acetyl derivative of **1**, with all three original stereocentres retained. This also accounts for the decrease from fifteen to fourteen carbons.

The subsequent operations erase and then restore the configuration at C8:

1. Hexamethyldisilazane/trimethylsilyl iodide gives the more substituted trimethylsilyl enol ether, placing the new double bond between C8 and the side-chain carbonyl carbon.
2. Methyllithium cleaves the silicon–oxygen bond, giving lithium enolate **3**.
3. Salicylic acid protonates that enolate stereoselectively.

The silyl enol ether is the **(Z)-trimethylsilyl enol ether of 2**:

`C[Si](C)(C)O/C(C)=C1/CCC2=CCC[C@@H](C)[C@]2(C)C1`

Intermediate **3**, the corresponding **lithium (Z)-enolate**, is:

`[Li+].[O-]/C(C)=C1/CCC2=CCC[C@@H](C)[C@]2(C)C1`

Formal net balances for these operations are

$$\mathrm{2\,C_{14}H_{22}O + C_6H_{19}NSi_2 \longrightarrow 2\,C_{17}H_{30}OSi + NH_3},$$
$$\mathrm{C_{17}H_{30}OSi + CH_3Li \longrightarrow C_{14}H_{21}LiO + Si(CH_3)_4},$$

and

$$\mathrm{C_{14}H_{21}LiO + C_7H_6O_3 \longrightarrow C_{14}H_{22}O + C_7H_5LiO_3}.$$

The last equation represents proton transfer from salicylic acid, `O=C(O)c1ccccc1O`, with formation of lithium salicylate.

Enolate formation makes C8 planar. Protonation occurs from the less hindered face, opposite the two methyl groups:

- For the valencene-derived enolate, the methyl groups point backward, so the incoming C8 hydrogen points forward. This gives the supplied ketone **4**, `CC(=O)[C@H]1CCC2=CCC[C@@H](C)[C@]2(C)C1`.
- For the eremophilene-derived enolate, the methyl groups point forward, so the incoming C8 hydrogen points backward. This gives **6**.

Thus **2 and 4 are C8 epimers**, whereas **6 and 4 are enantiomers**.

7.2 — Identification of the triflation reagent

Compound **7** is the terminal enol triflate of ketone **4**:

`C=C(OS(=O)(=O)C(F)(F)F)[C@H]1CCC2=CCC[C@@H](C)[C@]2(C)C1`

KHMDS removes a proton from the less hindered methyl side of the ketone at $-78\ ^\circ\mathrm{C}$. The resulting enolate must then receive a triflyl group at oxygen.

III, $\mathrm{PhNTf_2}$, is the suitable electrophilic triflyl-transfer reagent. Here Tf denotes $\mathrm{SO_2CF_3}$. Its reaction can be balanced generically as

$$\mathrm{RCOCH_3 + KN(SiMe_3)_2 + PhN(Tf)_2 \longrightarrow R{-}C(OTf){=}CH_2 + HN(SiMe_3)_2 + K[PhN(Tf)]}.$$

The bicyclic residue represented by R retains its configuration.

The other choices contain acidic O–H or N–H bonds and would primarily consume the strong base; they are not the appropriate triflyl-transfer reagent for this transformation.

7.3 — Alkyne formation, epoxidation, cyclopropenation and isotope tracing

Formation of 8. LDA causes elimination of triflate and a terminal vinylic hydrogen from **7**, giving the terminal alkyne **8**. The balanced generic reaction is

$$\mathrm{R{-}C(OTf){=}CH_2 + LiN(iPr)_2 \longrightarrow R{-}C{\equiv}CH + LiOTf + HN(iPr)_2}.$$

The product formula is $\mathrm{C_{14}H_{20}}$, whose nominal molar mass is

$$M \approx 14(12) + 20(1) = 188\ \mathrm{g\,mol^{-1}},$$

matching the supplied molecular weight.

Its degree of unsaturation is

$$\mathrm{DBE} = \frac{2(14) + 2 - 20}{2} = 5.$$

These five units are accounted for by two rings, one alkene and one alkyne. All three pre-existing stereocentres remain intact. An allene formed by removing the C8 hydrogen would destroy the C8 stereocentre and is excluded by the stated retention requirement.

Formation of 9 and 10. mCPBA epoxidizes the remaining ring alkene from either face. The terminal alkyne survives.

For either epoxide, the balanced oxygen-transfer reaction is

$$\mathrm{C_{14}H_{20} + C_7H_5ClO_3 \longrightarrow C_{14}H_{20}O + C_7H_5ClO_2}.$$

The two alkene carbons, C1 and C2, become new stereocentres. Therefore, each product has

$$3 + 2 = 5$$

stereocentres, as required. Neither contains a carbon–carbon double bond: the remaining unsaturation outside the rings is the alkyne.

We assign **9** to epoxidation from the front and **10** to epoxidation from the back. Their C5, C6 and C8 configurations remain those of **8**.

Formation of 11 and 12. The bromodifluoromethylsilane/iodide system generates difluorocarbene, $:\mathrm{CF_2}$, represented by `F[C]F`. It adds across the alkyne to produce a **3,3-difluorocyclopropene**:

$$\mathrm{C_{14}H_{20}O + CF_2 \longrightarrow C_{15}H_{20}F_2O}.$$

Including the silicon reagent, an overall atom balance is

$$\mathrm{C_{14}H_{20}O + (CH_3)_3SiCF_2Br \longrightarrow C_{15}H_{20}F_2O + (CH_3)_3SiBr}.$$

The original alkyne carbons become the two alkene carbons of the cyclopropene; the added carbene carbon bears both fluorine atoms. No existing stereocentre changes, so **11** retains the epoxide configuration of **9**, and **12** that of **10**.

Formation and labelling of 13 and 14. Acidic water performs two hydrolyses:

- The geminal difluoride becomes the cyclopropenone carbonyl. Its oxygen comes from water.
- The epoxide opens to a trans diol. One hydroxyl oxygen is the original epoxide oxygen; the other comes from water.

The balanced combined hydrolysis is

$$\mathrm{C_{15}H_{20}F_2O + 2\,H_2O \longrightarrow C_{15}H_{22}O_3 + 2\,HF}.$$

With $\mathrm{H_2\,^{18}O}$, both newly incorporated oxygen atoms are $^{18}\mathrm{O}$, so $n = 2$.

The stereochemistry of **15** fixes the diol geometry: C1–OH is forward and C2–OH is backward. The oxygen mapping therefore follows directly:

Product	C1 hydroxyl, forward	C2 hydroxyl, backward	Cyclopropenone carbonyl
13, from front epoxide **11**	Original $^{16}\mathrm{O}$	Incoming $^{18}\mathrm{O}$	Incoming $^{18}\mathrm{O}$
14, from back epoxide **12**	Incoming $^{18}\mathrm{O}$	Original $^{16}\mathrm{O}$	Incoming $^{18}\mathrm{O}$

For **11**, water attacks C2 from behind, breaking the C2–epoxide-oxygen bond. The original oxygen remains attached to C1.

For **12**, water attacks C1 from the front, breaking the C1–epoxide-oxygen bond. The original oxygen remains attached to C2.

Thus the products have identical constitution and stereochemistry after the isotope labels are removed, but the hydroxyl oxygen labels occupy different positions.

Consistency with ester 15. The catalyst is 4-(pyrrolidin-1-yl)pyridine, `c1cc(N2CCCC2)ccn1`. Methanol, CO, opens the cyclopropenone ring to give the methyl α-methylene ester **15**:

`COC(=O)C(=C)[C@H]1CC[C@@]2(O)[C@@H](O)CC[C@@H](C)[C@]2(C)C1`

Its name is **methyl 2-[(1S,2S,5R,6S,8S)-1,2-dihydroxy-5,6-dimethylbicyclo[4.4.0]decan-8-yl]prop-2-enoate**.

The balanced methanolysis is

$$\mathrm{C_{15}H_{22}O_3 + CH_3OH \longrightarrow C_{16}H_{26}O_4}.$$

The bond broken is between the cyclopropenone carbonyl carbon and the carbon derived from the terminal alkyne carbon. That latter carbon becomes the terminal methylene group. The carbonyl carbon becomes the ester carbonyl, and all five bicyclic stereocentres remain unchanged.

7.4 — Diphenylcyclopropenone and alcohol activation

Formation of 17. Starting compound **16** is **1,3-diphenylpropan-2-one**, or dibenzyl ketone:

`O=C(Cc1ccccc1)Cc1ccccc1`

Bromination under acidic conditions replaces one α-hydrogen on each side of the carbonyl:

$$\mathrm{PhCH_2COCH_2Ph + 2\,Br_2 \longrightarrow PhCHBrCOCHBrPh + 2\,HBr}.$$

This gives **17**, $\mathrm{C_{15}H_{12}Br_2O}$. Stereochemistry need not be specified.

Formation of 18. Base removes an α-hydrogen. Intramolecular displacement of bromide then creates a bond between the two α-carbons, forming a three-membered ring. Subsequent elimination of a second equivalent of hydrogen bromide gives diphenylcyclopropenone **18**.

The balanced equation is

$$\mathrm{C_{15}H_{12}Br_2O + 2\,Et_3N \longrightarrow C_{15}H_{10}O + 2\,Et_3NH^+ + 2\,Br^-}.$$

Cyclopropenone has an important charge-separated resonance contributor containing an aromatic cyclopropenium ring and negatively charged oxygen. For **18**, that contributor can be represented as

`[O-][C+]1C(c2ccccc2)=C1c1ccccc1`

The three-membered ring has two delocalized π electrons, satisfying Hückel's $4n + 2$ rule with $n = 0$.

Formation of 19. Thionyl chloride replaces the carbonyl oxygen by two chlorine atoms, giving the gem-dichloride **19**:

$$\mathrm{C_{15}H_{10}O + SOCl_2 \longrightarrow C_{15}H_{10}Cl_2 + SO_2}.$$

Loss of chloride from this reagent produces an aromatic cyclopropenium species, which explains its ability to activate an alcohol.

Formation and decomposition of 21. Alcohol **20** is **2-phenylethan-1-ol**, `OCCc1ccccc1`. Reaction with **19**, accompanied by loss of hydrogen chloride, gives alkoxycyclopropenium chloride **21**:

$$\mathrm{C_{15}H_{10}Cl_2 + C_8H_{10}O \longrightarrow [C_{23}H_{19}O]^+ + Cl^- + HCl}.$$

The NMR observations support this structure:

- Its three phenyl rings account for the **15 aromatic hydrogens**.
- The original hydroxyl proton is absent.
- The oxygen-bound methylene shifts from $\delta 3.7$ to $\delta 5.5\ \mathrm{ppm}$, consistent with attachment to the strongly electron-withdrawing cationic activating group.
- The benzylic methylene shifts from $\delta 2.8$ to $\delta 3.4\ \mathrm{ppm}$.

Chloride then attacks the primary carbon bonded to oxygen by an S_N2 displacement. Cleavage of that carbon–oxygen bond releases **2-phenylethyl chloride 22**, `ClCCc1ccccc1`, and regenerates diphenylcyclopropenone **18**:

$$\mathrm{[C_{23}H_{19}O]^+ + Cl^- \longrightarrow C_8H_9Cl + C_{15}H_{10}O}.$$

The overall alcohol-to-chloride conversion is therefore

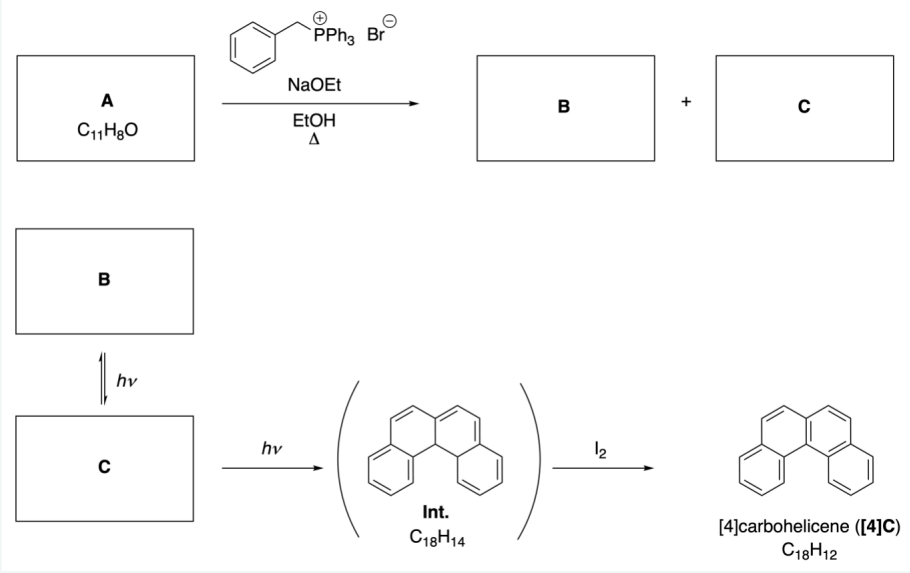
$$\mathrm{C_8H_{10}O + C_{15}H_{10}Cl_2 \longrightarrow C_8H_9Cl + C_{15}H_{10}O + HCl}.$$

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

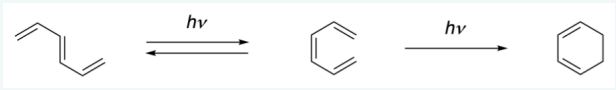
Problem 8: Dynamic Organic Molecules and Their Chirality

PART A

Polycyclic aromatic hydrocarbons with successive ortho-connections are called [n]carbohelicenes (here, n represents the number of six-membered rings) (see below). [4]Carbohelicene (**[4]C**) is efficiently prepared by a route using a photoreaction as shown below, via an intermediate (**Int.**) that is readily oxidized by iodine.



The photoreaction proceeds in a manner similar to the following example.

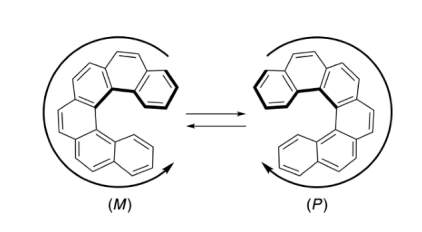


Note: For all of Question 8, please draw alternating single and double bonds in your answers to the problems as depicted in the examples of carbohelicene. Do not use circles for conjugated π systems.

8.1 Draw the structures of **A–C**. Stereoisomers should be distinguished.

8.2 Attempts to synthesize [5]carbohelicene from the same phosphonium salt and an appropriate starting compound resulted in the formation of only a trace amount of [5]carbohelicene, instead affording product **D** whose molecular weight was 2 Da lower than that of [5]carbohelicene. The $^1\mathrm{H}$ NMR chemical shifts of **D** are listed below. **Draw the structure of D.** [**D** (δ, ppm in $\mathrm{CS_2}$, r.t.), 8.85 (2H), 8.23 (2H), 8.07 (2H), 8.01 (2H), 7.97 (2H), 7.91 (2H)]

[5]- and larger [n]carbohelicenes have helical chirality and interconversion between enantiomers of these helicenes is significantly slow at room temperature. The chirality of [n]carbohelicenes is defined as (M) or (P) as shown below.

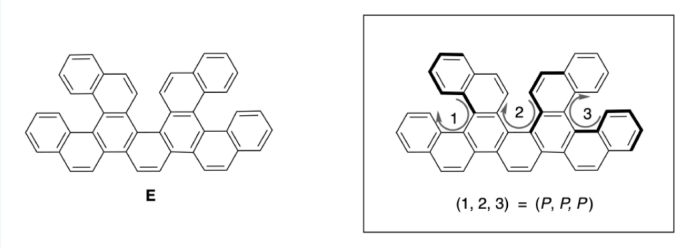


[n]Carbohelicenes with n larger than 4 can be enantiomerically separated by a chiral column chromatography, which was developed by Prof. Yoshio Okamoto.

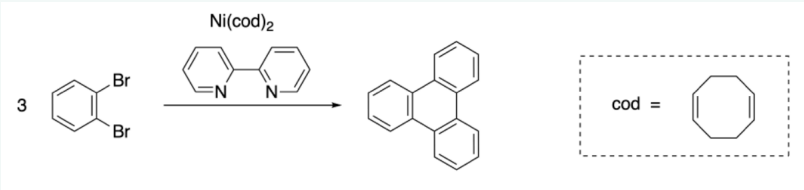


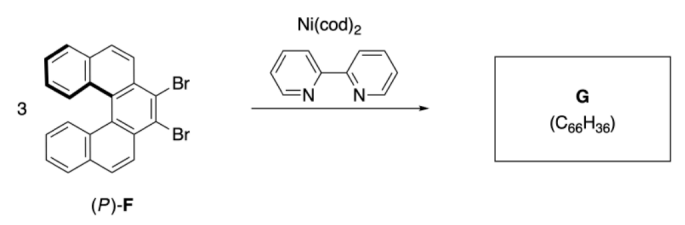
Photo courtesy: The Japan Prize Foundation

Multiple helicenes are molecules that contain two or more helicene-like structures. If its helical chirality is considered, several stereoisomers exist in a multiple helicene. For example, compound **E** contains three [5]carbohelicene-like moieties in one molecule. One of the stereoisomers is described as (P,P,P) as shown below.



8.3 The nickel-mediated trimerization of 1,2-dibromobenzene generates triphenylene. When the same reaction is applied to an enantiomer of **F**, (P)-**F**, multiple helicene **G** ($C_{66}H_{36}$) is obtained. Given that interconversion between stereoisomers does not occur during the reaction, identify all the possible stereoisomers of **G** formed in this process, without duplication. As a reference, one isomer should be drawn completely with the chirality defined as in the example above, with numerical labels; the other stereoisomers should be listed with location numbers and M and P labels according to the same numbering. For instance, the other stereoisomers of **E** should be listed as $(1,2,3) = (P,M,P)$, (P,M,M), (P,P,M), (M,M,M), (M,M,P), (M,P,P), and (M,P,M).



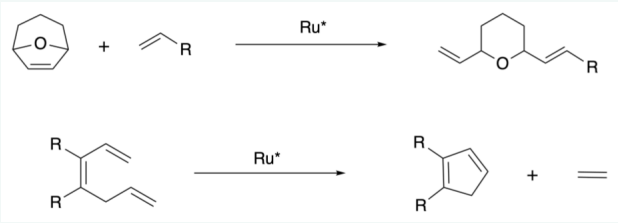


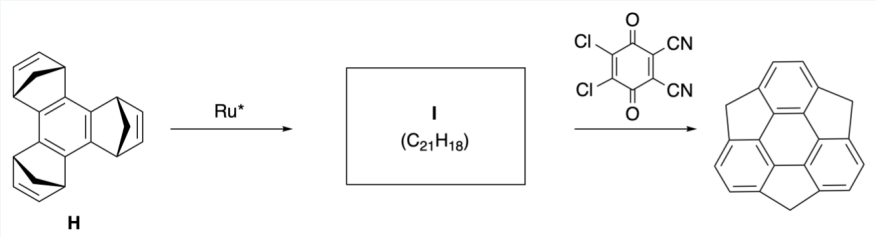
PART B

Sumanene is a bowl-shaped hydrocarbon that was first reported in Japan in 2003. The name "sumanene" derives from a Sanskrit-Hindi word "suman" that means sunflower. The synthesis of sumanene was achieved by a reaction sequence that consists of a ring-opening and a ring-closing metathesis.

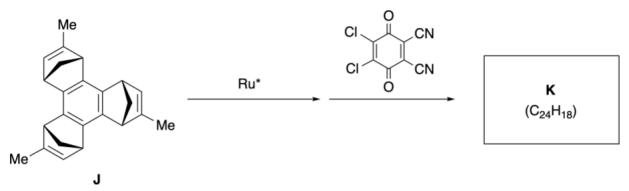


Representative metathesis reactions catalyzed by a ruthenium catalyst (Ru^*) are shown below.





8.4 Draw the structure of intermediate **I** (its stereochemistry is not required).



8.5 Starting from the optically active precursor **J**, the same reaction sequence gives the optically active sumanene derivative **K**. The stereocenters in **J** suffer no inversion during the metathesis reaction. Draw the structure of **K** with the appropriate stereochemistry.

Official English text of the problem.

Answers

All SMILES below use explicit Kekulé single and double bonds. Ordinary SMILES does not encode helicene handedness or bowl chirality; the accompanying spatial descriptions specify those configurations.

- **8.1**

A: Naphthalene-2-carbaldehyde, `O=CC1=CC2=CC=CC=C2C=C1`.

B: (E)-2-Styrylnaphthalene, `C1=CC=CC=C1/C=C/C1=CC2=CC=CC=C2C=C1`.

C: (Z)-2-Styrylnaphthalene, `C1=CC=CC=C1/C=C\C1=CC2=CC=CC=C2C=C1`.

- **8.2 D:** Benzo[ghi]perylene, $\mathrm{C_{22}H_{12}}$, `C1=CC2=CC=C3C=CC4=C5C6=C(C=CC=C6C(=C1)C2=C35)C=C4`.
- **8.3 G:** A hexapole [5]carbohelicene, $\mathrm{C_{66}H_{36}}$, with constitutional SMILES `C1=CC=C2C(=C1)C=CC1=C2C2=C3C=CC=CC3=CC=C2C2=C3C4=CC=C5C=CC=CC5=C4C4=C5C=CC=CC5=CC=C4C3=C3C4=CC=C5C=CC=CC5=C4C4=C`

Number its helicenes consecutively around the molecule, with **1, 3, 5 inherited from the three molecules of (P)-F**, and **2, 4, 6 newly formed between neighboring units**. There are **four** distinct products:

$$\begin{aligned}(1,2,3,4,5,6) = {} & (P,P,P,P,P,P),\\ & (P,P,P,P,P,M),\\ & (P,P,P,M,P,M),\\ & (P,M,P,M,P,M).\end{aligned}$$

- **8.4 I:** Hexahydrosumanene, $\mathrm{C_{21}H_{18}}$, `C1=CC2CC3C=CC4CC5C=CC6CC1C1=C2C3=C4C5=C16`.

It has the sumanene carbon skeleton, a central benzene ring, three methylene bridges, six saturated ring-junction CH groups, and one outer $\mathrm{C{=}C}$ bond in each peripheral six-membered ring.

- **8.5 K:** The specified bowl enantiomer of C_3-symmetric trimethylsumanene, $\mathrm{C_{24}H_{18}}$, with constitutional SMILES `CC1=CC2=C3C4=C1CC1=C4C4=C(CC5=C4C3=C(C2)C(C)=C5)C(C)=C1`.

Precise drawing: Look into the **concave face** of the bowl, with one peripheral benzene ring at the top. Put a methyl group on that ring's **upper-right outer carbon**, and obtain the other two methyl positions by successive 120° rotations. The three methylene rim vertices project toward the viewer relative to the central benzene.

Solution

8.1 — Identifying the aldehyde and the two alkene geometries

The phosphonium salt and sodium ethoxide constitute a Wittig reaction system. They convert an aldehyde group into a phenyl-substituted alkene:

$$\mathrm{C_{11}H_8O + [Ph_3PCH_2Ph]Br + NaOEt \longrightarrow C_{18}H_{14} + Ph_3PO + NaBr + EtOH.}$$

The $\mathrm{C_{18}H_{14}}$ product denotes the mixture of **B** and **C**, rather than two equivalents of product.

The species in this balance are benzyltriphenylphosphonium bromide, `[Br-].[P+](CC1=CC=CC=C1)(C1=CC=CC=C1)(C1=CC=CC=C1)C1=CC=CC=C1`; sodium ethoxide, `[Na+].CC[O-]`; triphenylphosphine oxide, `O=P(C1=CC=CC=C1)(C1=CC=CC=C1)C1=CC=CC=C1`; sodium bromide, `[Na+].[Br-]`; and ethanol, `CCO`.

Working backward from the illustrated four-ring product identifies the aromatic fragment as **2-naphthyl**. The newly formed ring joins naphthalene C1 to an ortho carbon of the phenyl ring; the original vinyl substituent is therefore at naphthalene C2. Thus **A is naphthalene-2-carbaldehyde**.

The two Wittig products differ in alkene geometry:

- In **B**, the naphthyl and phenyl groups are opposite across the double bond: E.
- In **C**, they are on the same side: Z.

Light interconverts these geometries. The Z isomer can adopt the geometry needed for a six-electron electrocyclic closure. The photochemical closure is conrotatory and produces the illustrated dihydro intermediate without changing its formula:

$$\mathrm{C_{18}H_{14} \xrightarrow{h\nu} C_{18}H_{14}.}$$

Here the reactant is **C**, and the product is dihydro[4]carbohelicene **Int.**, with constitutional SMILES `C1=CC2=CC=C3C=CC4=CC=CC=C4C3C2C=C1`.

Oxidation removes the two hydrogens at the newly connected carbons and restores the aromatic system:

$$\mathrm{C_{18}H_{14} + I_2 \longrightarrow C_{18}H_{12} + 2\,HI.}$$

Iodine is `II`; hydrogen iodide is `[H]I`. The product is **[4]carbohelicene**, also called **benzo[c]phenanthrene**, `C1=CC=C2C(=C1)C=CC1=C2C2=CC=CC=C2C=C1`.

8.2 — Identifying the additional oxidative cyclization product

An unmodified [n]carbohelicene has formula

$$\mathrm{C_{4n+2}H_{2n+4}}.$$

Consequently, [5]carbohelicene—pentahelicene, `C1=CC=C2C(=C1)C=CC1=C2C2=C(C=CC3=CC=CC=C32)C=C1`—has formula $\mathrm{C_{22}H_{14}}$.

A product lower in molecular mass by approximately $2\ \mathrm{Da}$, with the same carbon skeleton, corresponds to loss of two hydrogen atoms:

$$\mathrm{C_{22}H_{14} \longrightarrow C_{22}H_{12}}.$$

The hydrogen count is independently supported by the NMR integrations:

$$6 \times 2\mathrm{H} = 12\mathrm{H}.$$

The degrees of unsaturation are

$$\mathrm{DBE(C_{22}H_{14})} = \frac{2(22)+2-14}{2} = 16,$$

$$\mathrm{DBE(C_{22}H_{12})} = \frac{2(22)+2-12}{2} = 17.$$

Thus one additional ring can form through a new carbon–carbon bond between the closely approaching terminal regions of the five-ring helicene, followed by oxidative loss of two hydrogens. This produces **benzo[ghi]perylene D**, a planar, six-ring aromatic hydrocarbon.

The formal iodine-mediated oxidative balance is

$$\mathrm{C_{22}H_{14} + I_2 \longrightarrow C_{22}H_{12} + 2\,HI.}$$

Drawing description: Begin with [5]carbohelicene and connect the two inward-facing terminal carbons that close its remaining central six-membered bay. Remove their hydrogens and draw a valid Kekulé pattern.

The resulting structure has **six symmetry-related pairs of proton-bearing carbons**, consistent with the six reported resonances, each integrating to two hydrogens. Individual assignment of the six chemical shifts is unnecessary for identifying **D**.

8.3 — Constructing G and removing duplicate stereoisomers

The nickel-mediated reaction joins the six bromine-bearing carbon atoms of three starting molecules into a central benzene ring. A formal balance, omitting the ligands, is

$$\mathrm{3\,C_{22}H_{12}Br_2 + 3\,Ni \longrightarrow C_{66}H_{36} + 3\,NiBr_2}.$$

Nickel(0) is `[Ni]`; nickel(II) bromide is `[Ni+2].[Br-].[Br-]`.

The starting compound is the depicted dibromo[5]carbohelicene **F**, with constitutional SMILES `BrC1=C(Br)C2=C(C3=CC=CC=C3C=C2)C2=C1C=CC1=CC=CC=C12`; its helicity is explicitly P.

The construction parallels formation of **triphenylene**, `C1=CC=C2C(=C1)C1=CC=CC=C1C1=CC=CC=C21`, but each of its three outer fused rings now carries the remaining four rings of a starting helicene.

Complete reference-structure description: Draw a central benzene ring. Fuse the middle ring of each of three [5]carbohelicene units to alternate edges of this central ring, using the former bromine-bearing edge of each unit. This gives the connectivity specified by the SMILES for **G**. The product contains six [5]helicene substructures.

Call the three starting units X_1, X_2, X_3, in clockwise order, and number the helicenes as follows:

Label	Helical substructure
1	Original helicene within X_1
2	Newly formed helicene between X_1 and X_2
3	Original helicene within X_2
4	Newly formed helicene between X_2 and X_3
5	Original helicene within X_3
6	Newly formed helicene between X_3 and X_1

For the reference drawing, mark all six helicenes P: each is a right-handed helix.

Because inversion does not occur, helicenes **1, 3, 5 remain** P. Each of the three new helicenes may be P or M, giving $2^3 = 8$ labeled possibilities.

However, cyclic rotation of the three identical starting units makes several labeled assignments equivalent. The distinct classes contain:

1. No new M helices.
2. One new M helix.
3. Two new M helices.
4. Three new M helices.

Equivalently, counting configurations under the threefold rotation gives

$$N = \frac{8+2+2}{3} = \boxed{4}.$$

These are exactly the four configurations listed in **Answers**.

8.4 — Following the metathesis rearrangement

The ruthenium-catalyzed sequence changes connectivity while conserving the molecular formula:

$$\underbrace{\mathrm{C_{21}H_{18}}}_{\mathrm{H}} \xrightarrow{\mathrm{Ru^*}} \underbrace{\mathrm{C_{21}H_{18}}}_{\mathrm{I}}.$$

Each original bicyclic unit contains a methylene bridge and an outer alkene. Ring-opening metathesis breaks the original outer alkene connections; ring-closing metathesis reconnects neighboring units.

More explicitly, label the three original outer double bonds $p_i = q_i$, with $i = 1, 2, 3$ in clockwise order. The rearrangement replaces them with $q_i = p_{i+1}$, taking indices modulo three. The three methylene bridges are retained and become the methylene vertices of the three five-membered rings.

This produces **hexahydrosumanene I**.

Drawing description: Start with the sumanene skeleton shown in the question. Keep the central benzene ring and all three methylene vertices. In each peripheral six-membered ring:

- Make its two junction carbons adjoining the neighboring pentagons saturated CH groups.
- Retain a double bond between its two outer, nonfused carbon atoms.

A Kekulé drawing can therefore show each peripheral six-membered ring as a substituted cyclohexa-1,4-diene unit.

The hydrogen count verifies the proposed intermediate:

$$3(\mathrm{CH_2}) + 6(\text{saturated } \mathrm{CH}) + 6(\text{alkenic } \mathrm{CH}) \quad \Rightarrow \quad \mathrm{C_{21}H_{18}},$$

including the six hydrogen-free carbons of the central benzene ring.

The oxidant is **DDQ**, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, `N#CC1=C(C#N)C(=O)C(Cl)=C(Cl)C1=O`. Each molecule accepts two hydrogen atoms. Aromatization of all three peripheral rings therefore requires three equivalents:

$$\mathrm{C_{21}H_{18}} + 3\,\mathrm{C_8Cl_2N_2O_2} \longrightarrow \mathrm{C_{21}H_{12}} + 3\,\mathrm{C_8H_2Cl_2N_2O_2}.$$

The hydrocarbon product is **sumanene**, `C1=CC2=C3C4=C1CC1=C4C4=C(C=C1)CC1=C4C3=C(C=C1)C2`.

The reduced oxidant is **2,3-dichloro-5,6-dicyanobenzene-1,4-diol**, `N#CC1=C(C#N)C(O)=C(Cl)C(Cl)=C1O`.

8.5 — Tracking the methyl groups and bowl handedness

In **J**, each methyl group is attached to an outer alkene carbon. Consequently, the methyl groups remain attached to carbons that become part of the three peripheral aromatic rings.

For an explicit stereochemical reference, the drawn trimethylated bridged precursor **J** has isomeric SMILES:

`CC1=C[C@@H]2C[C@H]1C1=C2C2=C(C3=C1[C@@H]1C=C(C)[C@H]3C1)[C@@H]1C=C(C)[C@H]2C1`.

The formula changes are

$$\underbrace{\mathrm{C_{24}H_{24}}}_{\mathrm{J}} \xrightarrow{\mathrm{Ru^*}} \underbrace{\mathrm{C_{24}H_{24}}}_{\text{rearranged intermediate}},$$

followed by

$$\mathrm{C_{24}H_{24}} + 3\,\mathrm{C_8Cl_2N_2O_2} \longrightarrow \mathrm{C_{24}H_{18}} + 3\,\mathrm{C_8H_2Cl_2N_2O_2}.$$

The final formula also follows directly from replacing three aromatic hydrogens of sumanene by methyl groups:

$$\mathrm{C_{21}H_{12}} + 3(\mathrm{CH_3} - \mathrm{H}) \quad \Rightarrow \quad \mathrm{C_{24}H_{18}}.$$

To determine the enantiomer, retain the configurations of all six original bridgeheads during the metathesis bond reconnections. In the upper bicyclic unit of the supplied drawing, the methyl-bearing alkene carbon is attached to the upper-right bridgehead. Tracking this carbon through the neighboring-ring closure gives the following equivalent projections of **K**:

- **Viewed from the convex face:** with one peripheral benzene at the top, its methyl is at the upper-left outer carbon.
- **Viewed into the concave face:** the same methyl is at the upper-right outer carbon.

The other two methyl groups follow by 120° rotations. This specifies the bowl enantiomer obtained from the drawn **J**.

Oxidation converts the six retained bridgehead stereocenters into trigonal aromatic carbons. The final chirality resides in the bowl together with its directional threefold methyl-substitution pattern; it is therefore specified by the spatial description rather than by tetrahedral `@` symbols in the SMILES for **K**.

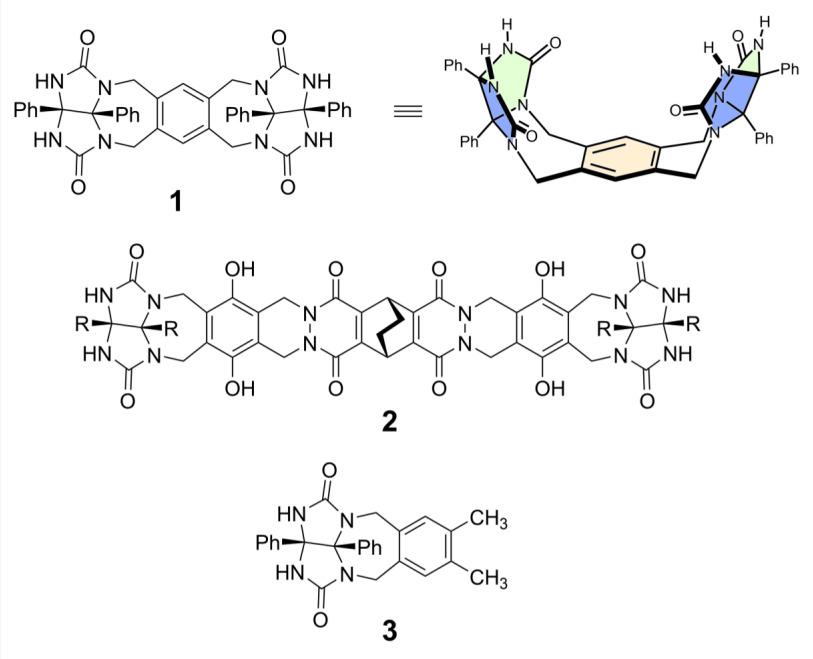
The answers were checked against the official answers published by the organisers.

Problem 9: Likes and Dislikes of Capsule

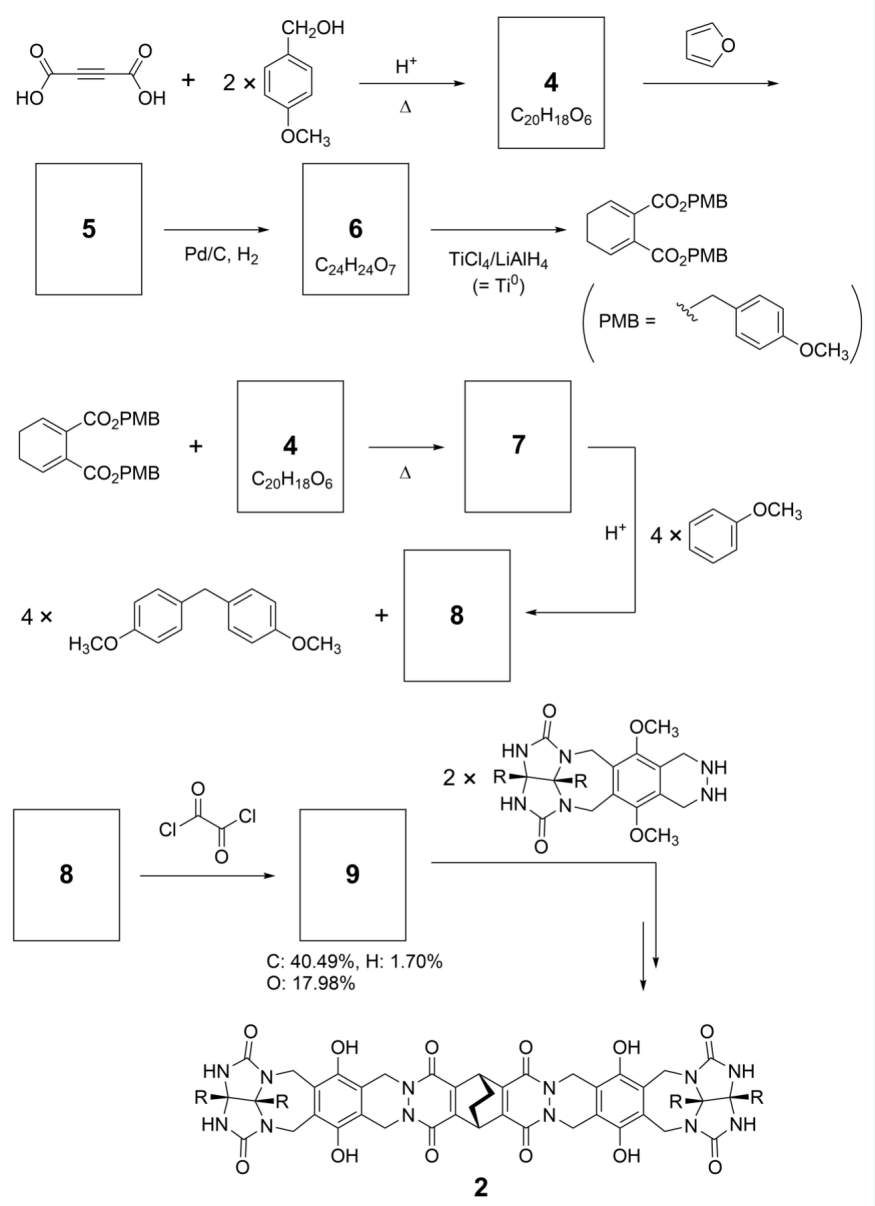
> Good kids don't do this, but if you unseam a tennis ball, you can disassemble it into two U-shaped pieces.



Based on this idea, compounds **1** and **2** were synthesized as U-shaped molecules with different sizes. Compound **3** was prepared as a comparison of **1** and the encapsulation behavior of these compounds was investigated.



The synthetic route to **2** is shown below. The elemental composition of compound **9**: C; 40.49%, H; 1.70%, and O; 17.98% by mass.



9.1 Draw the structures of **4–9**; the stereochemistry can be neglected. Use "PMB" as a substituent instead of drawing the whole structure of *p*-methoxybenzyl group shown in the scheme above.

In the mass spectrum of **1**, the ion peak corresponding to its dimer ($\mathbf{1}_2$) was clearly observed, whereas an ion peak for $\mathbf{3}_2$ was not observed in the spectrum of **3**. In the $^1\mathrm{H}$ NMR spectra of a solution of $\mathbf{1}_2$, all the NH protons derived from **1** were observed to be chemically equivalent, and their chemical shift was significantly different from that of the NH protons of **3**. These data indicate that hydrogen bonds are formed between the NH moieties of **1** and atoms **X** of another molecule of **1** to form the dimeric capsule.

9.2 Circle all the appropriate atom(s) **X** in **1**.

9.3 Give the number of the hydrogen bonds in the dimeric capsule ($\mathbf{1}_2$).

The dimeric capsule of **1** ($\mathbf{1}_2$) has an internal space wherein an appropriate small molecule Z can be encapsulated. This phenomenon is expressed by the following equation:

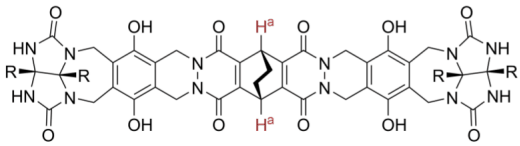
$$\mathrm{Z} + \mathbf{1}_2 \longrightarrow \mathrm{Z}@\mathbf{1}_2 \tag{1}$$

The equilibrium constant of the encapsulation of Z into $\mathbf{1}_2$ is given as below:

$$K_a = \frac{[\mathrm{Z}@\mathbf{1}_2]}{[\mathrm{Z}][\mathbf{1}_2]} \tag{2}$$

Encapsulation of a molecule into a capsule could be monitored by NMR spectroscopy. For example, $\mathbf{1}_2$ in $\mathrm{C_6D_6}$ gave different signals in the $^1\mathrm{H}$ NMR spectra before and after addition of $\mathrm{CH_4}$.

Compound **2** also forms a rigid and larger dimeric capsule ($\mathbf{2}_2$). The $^1\mathrm{H}$ NMR spectrum of $\mathbf{2}_2$ was measured in $\mathrm{C_6D_6}$, $\mathrm{C_6D_5F}$, and a $\mathrm{C_6D_6/C_6D_5F}$ solvent mixture, with all other conditions being kept constant. The chemical shifts for the H^a proton of **2** in the above solvents are summarized below, and no other signals from the H^a in **2**, except for the listed, were observed. Assume that the interior of the capsule is always filled with the largest possible number of solvent molecules and that each signal corresponds to one species of the filled capsule.



2

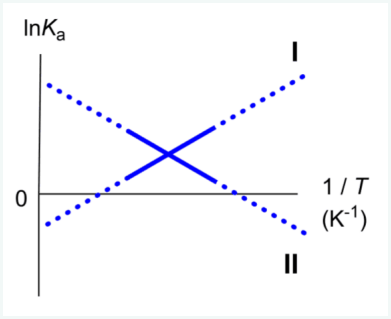
solvent	δ (ppm) of H^{a}
$\mathrm{C_6D_6}$	4.60
$\mathrm{C_6D_5F}$	4.71
$\mathrm{C_6D_6/C_6D_5F}$	4.60, 4.71, 4.82

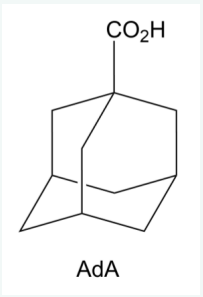
9.4 Determine the number of $\mathrm{C_6D_6}$ and $\mathrm{C_6D_5F}$ molecules encapsulated in $\mathbf{2}_2$ giving each H^{a} signal.

$^1\mathrm{H}$ NMR measurements in $\mathrm{C_6D_6}$ revealed that $\mathbf{2}_2$ can incorporate one molecule of 1-adamantanecarboxylic acid (AdA), and the association constants (K_a) which are expressed below were determined for various temperatures. $[\mathrm{solvent@}\mathbf{2}_2]$ denotes a species containing one or more solvent molecules.

$$K_a = \frac{[\mathrm{Z@}\mathbf{2}_2]}{[\mathrm{Z}][\mathrm{solvent@}\mathbf{2}_2]} \tag{3}$$

Similarly, the K_a values of $\mathrm{CH_4}$ and $\mathbf{1}_2$ given as eq (2) at various temperatures in $\mathrm{C_6D_6}$ were also determined by $^1\mathrm{H}$ NMR measurements. The plots of the two association constants (as $\ln K_a$ vs $1/T$) are shown below.





No $\mathrm{C_6D_6}$ molecule is encapsulated in $\mathbf{1}_2$. In line **II**, the entropy change (ΔS) is (1) and enthalpy change (ΔH) is (2), indicating that the driving force for the encapsulation in line **II** is (3). Therefore, line **I** corresponds to (4), and line **II** corresponds to (5).

9.5 Choose the correct options in gaps (1)–(5) in the following paragraph from A and B.

	A	B
(1)	positive	negative
(2)	positive	negative
(3)	ΔS	ΔH
(4)	$\mathbf{1}_2$ and $\mathrm{CH_4}$	$\mathbf{2}_2$ and AdA
(5)	$\mathbf{1}_2$ and $\mathrm{CH_4}$	$\mathbf{2}_2$ and AdA

Official English text of the problem.

Answers

- **9.1:** The structures are listed below. In the requested drawings, retain the abbreviation **PMB** for the *p*-methoxybenzyl group. The SMILES expand PMB to give complete connectivity; stereochemistry is omitted as permitted.

Compound	Name	SMILES
4	Bis(4-methoxybenzyl) but-2-ynedioate	`COc1ccc(COC(=O)C#CC(=O)OCc2ccc(OC)cc2)cc1`
5	Bis(4-methoxybenzyl) 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate	`C1(C(=O)OCc2ccc(OC)cc2)=C(C(=O)OCc2ccc(OC)cc2)C2C=CC1O2`
6	Bis(4-methoxybenzyl) 7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate	`C1(C(=O)OCc2ccc(OC)cc2)=C(C(=O)OCc2ccc(OC)cc2)C2CCC1O2`
7	Tetrakis(4-methoxybenzyl) bicyclo[2.2.2]octa-2,5-diene-2,3,5,6-tetracarboxylate	`C1(C(=O)OCc2ccc(OC)cc2)=C(C(=O)OCc2ccc(OC)cc2)C2CCC1C(C(=O)OCc1ccc(OC)cc1)=C2C(=O)OCc1ccc(OC)cc1`
8	Bicyclo[2.2.2]octa-2,5-diene-2,3,5,6-tetracarboxylic acid	`C1(C(=O)O)=C(C(=O)O)C2CCC1C(C(=O)O)=C2C(=O)O`

Compound	Name	SMILES
9	Bicyclo[2.2.2]octa-2,5-diene-2,3,5,6-tetracarbonyl tetrachloride	`C1(C(=O)Cl)=C(C(=O)Cl)C2CCC1C(C(=O)Cl)=C2C(=O)Cl`

- **9.2:** Circle **all four carbonyl oxygen atoms** of **1**: the two carbonyl oxygens in each terminal glycoluril unit.
- **9.3:** The dimeric capsule contains **8 hydrogen bonds**.
- **9.4:** Each capsule contains **two solvent molecules**.

$\delta(\mathrm{H}^a)$ / ppm	Number of $\mathrm{C_6D_6}$ molecules	Number of $\mathrm{C_6D_5F}$ molecules
4.60	2	0
4.71	0	2
4.82	1	1

The guests are benzene-d_6, `[2H]c1c([2H])c([2H])c([2H])c([2H])c1[2H]`, and fluorobenzene-d_5, `Fc1c([2H])c([2H])c([2H])c([2H])c1[2H]`.

- **9.5: (1) A; (2) A; (3) A; (4) A; (5) B.**

Thus line **II** has $\Delta S > 0$, $\Delta H > 0$, and is entropy-driven. Line **I** represents methane, `C`, binding to $\mathbf{1}_2$. Line **II** represents adamantane-1-carboxylic acid, `O=C(O)C12CC3CC(CC(C3)C1)C2`, binding to $\mathbf{2}_2$.

Solution

9.1 — Identification of compounds 4–9

The PMB group is *p*-methoxybenzyl, represented as the fragment `*Cc1ccc(OC)cc1`, where `*` marks its attachment to the rest of the structure.

Esterification gives 4. The starting materials are but-2-ynedioic acid, also called acetylenedicarboxylic acid, `O=C(O)C#CC(=O)O`, and 4-methoxybenzyl alcohol, `COc1ccc(CO)cc1`. Both carboxylic acid groups undergo acid-catalysed esterification:

$$\mathrm{C_4H_2O_4} + 2\,\mathrm{C_8H_{10}O_2} \xrightarrow{\mathrm{H^+},\ \Delta} \mathrm{C_{20}H_{18}O_6} + 2\,\mathrm{H_2O}.$$

Thus **4** is the di-PMB ester of acetylenedicarboxylic acid. Its molecular formula agrees with the supplied $\mathrm{C_{20}H_{18}O_6}$.

For the drawing, place a triple bond between the two central carbon atoms, with a $-\mathrm{C(=O)O-PMB}$ group at each end.

A Diels–Alder reaction with furan gives 5. Furan, `c1ccoc1`, supplies the four-atom diene, while the activated alkyne of **4** is the dienophile:

$$\mathrm{C_{20}H_{18}O_6} + \mathrm{C_4H_4O} \longrightarrow \mathrm{C_{24}H_{22}O_7}.$$

The cycloaddition forms two new carbon–carbon σ bonds. One double bond remains between the two alkyne-derived carbon atoms, and another remains between the two internal carbons of the original furan diene. The furan oxygen becomes the one-atom bridge.

Consequently, **5** has a 7-oxabicyclo[2.2.1]hepta-2,5-diene skeleton, with the two ester groups on the same double bond.

Hydrogenation gives 6. The supplied formula changes from $\mathrm{C_{24}H_{22}O_7}$ to $\mathrm{C_{24}H_{24}O_7}$, so exactly one equivalent of hydrogen is added:

$$\mathrm{C_{24}H_{22}O_7} + \mathrm{H_2} \xrightarrow{\mathrm{Pd/C}} \mathrm{C_{24}H_{24}O_7}.$$

The double bond without ester substituents is hydrogenated. The ester-bearing double bond remains, as required for the subsequent formation of the depicted conjugated diene.

To draw **5** and **6** precisely, connect two bridgehead CH groups by three paths:

- An oxygen bridge, $-\mathrm{O}-$.
- An ester-bearing alkene bridge, $-\mathrm{C(CO_2PMB)=C(CO_2PMB)}-$.
- A $-\mathrm{CH=CH}-$ bridge in **5**, replaced by $-\mathrm{CH_2-CH_2}-$ in **6**.

Removal of the oxygen bridge gives the depicted conjugated diene. Reduced titanium removes the bridging oxygen, with rearrangement of the carbon–carbon double bonds. The product is bis(4-methoxybenzyl) cyclohexa-1,3-diene-2,3-dicarboxylate:

`C1=C(C(=O)OCc2ccc(OC)cc2)C(C(=O)OCc2ccc(OC)cc2)=CCC1`

Its formula is $\mathrm{C_{24}H_{24}O_6}$. Because the problem does not specify the titanium-containing coproducts, the organic reduction can be balanced formally as the half-reaction

$$\mathrm{C_{24}H_{24}O_7} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{C_{24}H_{24}O_6} + \mathrm{H_2O}.$$

This equation is atom and charge bookkeeping; it does not imply an aqueous acidic reaction medium. In the actual transformation, reduced titanium accepts the oxygen.

A second Diels–Alder reaction gives 7. The conjugated diene reacts with another molecule of alkyne **4**:

$$\mathrm{C_{24}H_{24}O_6} + \mathrm{C_{20}H_{18}O_6} \xrightarrow{\Delta} \mathrm{C_{44}H_{42}O_{12}}.$$

The two saturated carbons of the original six-membered ring become one ethylene bridge of a bicyclo[2.2.2]octadiene framework. The remaining two bridges each contain a double bond, and every carbon of these two double bonds bears an ester group.

Therefore **7** is the tetra-PMB ester of bicyclo[2.2.2]octa-2,5-diene-2,3,5,6-tetracarboxylic acid.

Acidic PMB cleavage gives 8. The four PMB ester groups are removed. Anisole, `COc1ccccc1`, traps the benzyl electrophile released from each protecting group. The depicted trapping product is bis(4-methoxyphenyl)methane:

`COc1ccc(Cc2ccc(OC)cc2)cc1`

The balanced overall equation is

$$\mathrm{C_{44}H_{42}O_{12}} + 4\,\mathrm{C_7H_8O} \xrightarrow{\mathrm{H^+}} \mathrm{C_{12}H_{10}O_8} + 4\,\mathrm{C_{15}H_{16}O_2}.$$

Thus **8** is the tetracarboxylic acid, $\mathrm{C_{12}H_{10}O_8}$. The bicyclic carbon skeleton and both double bonds remain unchanged.

Oxalyl chloride gives 9. Oxalyl chloride, `O=C(Cl)C(=O)Cl`, converts each of the four carboxylic acid groups into an acid chloride:

$$\mathrm{C_{12}H_{10}O_8} + 4\,\mathrm{C_2Cl_2O_2} \longrightarrow \mathrm{C_{12}H_6Cl_4O_4} + 4\,\mathrm{CO} + 4\,\mathrm{CO_2} + 4\,\mathrm{HCl}.$$

For the drawings of **7–9**, connect two bridgehead CH groups by three two-carbon bridges. One is $-\mathrm{CH_2}-\mathrm{CH_2}^-$; the other two are each $-\mathrm{C(Q)}=\mathrm{C(Q)}^-$, with:

Compound	Q
7	$-\mathrm{C(=O)O-PMB}$
8	$-\mathrm{C(=O)OH}$
9	$-\mathrm{C(=O)Cl}$

This specifies the requested structures without assigning stereochemistry.

The elemental analysis independently confirms **9**. The remaining mass percentage is chlorine:

$$w_{\mathrm{Cl}} = 100.00 - 40.49 - 1.70 - 17.98 = 39.83\%.$$

For a $100.00\ \mathrm{g}$ sample, using atomic molar masses 12.01, 1.008, 16.00, and $35.45\ \mathrm{g\,mol^{-1}}$,

$$n_{\mathrm{C}} = \frac{40.49}{12.01} = 3.371\ \mathrm{mol},$$
$$n_{\mathrm{H}} = \frac{1.70}{1.008} = 1.687\ \mathrm{mol},$$
$$n_{\mathrm{O}} = \frac{17.98}{16.00} = 1.124\ \mathrm{mol},$$
$$n_{\mathrm{Cl}} = \frac{39.83}{35.45} = 1.124\ \mathrm{mol}.$$

Hence

$$n_{\mathrm{C}} : n_{\mathrm{H}} : n_{\mathrm{O}} : n_{\mathrm{Cl}} \simeq 3 : 1.5 : 1 : 1 = 6 : 3 : 2 : 2.$$

The empirical formula is $\mathrm{C_6H_3Cl_2O_2}$. The known twelve-carbon skeleton requires twice this formula:

$$\boxed{\mathrm{C_{12}H_6Cl_4O_4}}.$$

Its calculated molar mass is $355.97\ \mathrm{g\,mol^{-1}}$, giving

$$w_{\mathrm{C}} = 40.49\%, \qquad w_{\mathrm{H}} = 1.70\%, \qquad w_{\mathrm{O}} = 17.98\%,$$

in agreement with every supplied percentage.

The small molecular species in the equations are water, `O`; hydrogen, `[H][H]`; carbon monoxide, `[C-]#[O+]`; carbon dioxide, `O=C=O`; and hydrogen chloride, `Cl`.

9.2 — Hydrogen-bond acceptors

Host **1** is the benzene-linked bis(diphenylglycoluril) host shown in the statement. Its covalent connectivity is:

```
O=C1NC2(c3ccccc3)NC(=O)N3Cc4cc5c(cc4CN1C23c1ccccc1)CN1C(=O)NC2(c3ccccc3)NC(=O)N(C5)C12c1ccccc1
```

Its U-shaped geometry is specified by the supplied drawing; a connectivity SMILES does not describe the capsule's conformation or hydrogen-bond network.

Each glycoluril unit contains two urea carbonyl groups. Their oxygen atoms possess lone pairs that can accept hydrogen bonds from the NH groups of the other monomer:

$$\mathrm{N-H\cdots O=C}.$$

The urea nitrogen lone pairs are delocalized into the carbonyl groups, so these nitrogens are not the appropriate hydrogen-bond acceptors.

Therefore, circle **the four carbonyl oxygen atoms**, namely the upper and lower carbonyl oxygens at each end of **1**.

9.3 — Number of hydrogen bonds

Each molecule of **1** contains:

- Four NH hydrogen-bond donors.
- Four carbonyl-oxygen hydrogen-bond acceptors.

The dimer therefore has eight NH donors. In the closed capsule, each NH group donates one hydrogen bond to a carbonyl oxygen on the other monomer:

$$N_{\text{hydrogen bonds}} = 2 \times 4 = \boxed{8}.$$

This counts eight distinct donor–acceptor contacts, rather than counting both ends of a hydrogen bond separately. The equivalent hydrogen-bonded environments also account for the equivalent NH signals described in the problem.

9.4 — Solvent occupancy

Host **2** is the larger bis(glycoluril) host drawn in the statement. Its generic connectivity SMILES is given below, with each `*` representing one unspecified R substituent:

```
C1(C(=O)N3N(C9=O)Cc4c(O)c5c(c(O)c4C3)CN3C(=O)NC4(*)NC(=O)N(C5)C34*)=C9C2CCC1C(C(=O)N3N(C%10=O)Cc4c(O)c5c(c(O)c4C3)CN3C(
```

Each capsule contains two such host molecules. Their spatial arrangement and the location of guests inside the cavity must be specified in words; ordinary SMILES does not encode encapsulation.

Let B denote benzene-d_6 and F fluorobenzene-d_5, whose SMILES are given in the Answers section.

For a capsule filled with n solvent molecules, the possible guest compositions are

$$B_n,\ B_{n-1}F,\ B_{n-2}F_2, \ldots, F_n.$$

There are $n+1$ compositions. Under the problem's stated signal-counting model, the three observed signals imply

$$n+1=3 \quad \Longrightarrow \quad \boxed{n=2}.$$

The pure-solvent measurements identify the two homogeneous occupancies:

$$\begin{aligned} 4.60\ \text{ppm}: &\quad B_2@\mathbf{2}_2, \\ 4.71\ \text{ppm}: &\quad F_2@\mathbf{2}_2. \end{aligned}$$

The remaining signal must correspond to the mixed pair:

$$4.82\ \text{ppm}: \quad BF@\mathbf{2}_2.$$

Thus the guest counts are respectively $(2,0)$, $(0,2)$, and $(1,1)$. No assumption that the mixed capsule's chemical shift is an average of the other two shifts is needed.

9.5 — Thermodynamic signs and identification of the lines

Using the fixed standard-state convention implicit in the plotted association constants, the van 't Hoff relation is

$$\ln K_a = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R}.$$

Consequently,

$$\text{slope} = -\frac{\Delta H}{R}, \qquad \text{vertical intercept} = \frac{\Delta S}{R}.$$

For line **II**, the slope is negative and the vertical intercept is positive. Therefore,

$$\boxed{\Delta H_{\mathrm{II}} > 0}, \qquad \boxed{\Delta S_{\mathrm{II}} > 0}.$$

Since

$$\Delta G = \Delta H - T\Delta S,$$

the positive enthalpy change opposes binding, while the positive entropy change supplies the favorable contribution. Line **II** is therefore **entropy-driven**.

The two encapsulation processes explain the assignments.

For methane, the smaller capsule initially contains no benzene-d_6:

$$\mathrm{CH_4} + \mathbf{1}_2 \rightleftharpoons \mathrm{CH_4}@\mathbf{1}_2.$$

Binding restricts the guest's translational and rotational freedom, without releasing an encapsulated solvent molecule. This is consistent with the negative entropy change of line **I**, whose negative intercept and positive slope indicate

$$\Delta S_{\mathrm{I}} < 0, \qquad \Delta H_{\mathrm{I}} < 0.$$

For adamantane-1-carboxylic acid, one guest replaces the two benzene-d_6 molecules inside the larger capsule:

$$\mathrm{C_{11}H_{16}O_2} + (\mathrm{C_6D_6})_2@\mathbf{2}_2 \rightleftharpoons \mathrm{C_{11}H_{16}O_2}@\mathbf{2}_2 + 2\mathrm{C_6D_6}.$$

Release of two confined solvent molecules into the bulk solvent provides an entropy gain that can outweigh the entropy loss associated with binding one acid molecule. This explains the entropy-driven process represented by line **II**.

The completed choices are therefore:

Gap	Result	Option
(1)	Positive ΔS	**A**
(2)	Positive ΔH	**A**
(3)	Entropy, ΔS, is the driving force	**A**
(4)	$\mathbf{1}_2$ and methane	**A**
(5)	$\mathbf{2}_2$ and adamantane-1-carboxylic acid	**B**

The solution was checked against the official solution.