IChO 2024

Theory problems and solutions · Riyadh, Saudi Arabia · 9 theory problems with complete solutions

Problem 1: Ammonia

The Haber–Bosch process to produce ammonia from nitrogen and hydrogen is one of the most impactful industrial processes in history and estimated to sustain around half of today's population. The process typically occurs at constant temperature and pressure, 400 °C and 100 bar, respectively. Equilibrium between the reactants and the product is established over Fe-based catalysts in the reactor.

The standard gas phase thermochemistry data of $\mathrm{N_2}$, $\mathrm{H_2}$, and $\mathrm{NH_3}$ are shown below. Assume the enthalpy and entropy of the reaction are temperature independent.

	$\mathrm{N_2\,(g)}$	$\mathrm{H_2\,(g)}$	$\mathrm{NH_3\,(g)}$
$\Delta_f H^\circ / (\mathrm{kJ\,mol^{-1}})$	0	0	−45.9
$S^\circ / (\mathrm{J\,mol^{-1}\,K^{-1}})$	191.6	130.7	192.8

1.1 — 7 pt

Find the molar nitrogen conversion (in percent) to ammonia under the production conditions from a stoichiometric mixture of nitrogen and hydrogen. Show your calculations for partial credit. *If you cannot find a result, use 66% in subsequent calculations.*

One of the reactants in the Haber–Bosch process is hydrogen, mainly produced by steam reforming of methane. The two-step process starts with $\mathrm{CH_4}$ reacting with water to produce $\mathrm{H_2}$ and CO. In a subsequent step, CO reacts with water to form $\mathrm{CO_2}$ and additional hydrogen.

1.2 — 2 pt

Write the overall reaction equation for the combined process. **Give** the mass of $\mathrm{CO_2}$ produced in the reaction per 1.0 kg of $\mathrm{H_2}$ ($m_{\mathrm{CO_2}}$).

In reality, 7.0 kg of carbon dioxide is produced for each 1.0 kg of hydrogen in steam reforming. The generated ammonia is classified based on $\mathrm{CO_2}$ management. For "gray" ammonia, the $\mathrm{CO_2}$ is released in the atmosphere; for "blue" ammonia, it is captured and stored. "Green" ammonia is made from hydrogen produced without carbon emissions.

1.3 — 3 pt

Calculate the mass of the carbon dioxide ($m_{\mathrm{CO_2,\,blue}}$) that needs to be captured to produce 40,000 kg of "blue" ammonia. Assume that carbon dioxide only comes from a real steam reforming process. Assume further that the ammonia is produced at equilibrium from a stoichiometric mixture of nitrogen and hydrogen.

Using cheap renewable hydrogen, the prospect of converting it with captured $\mathrm{CO_2}$ into methanol appears promising. However, in this procedure, there is a competing reaction that produces CO:

$$\mathrm{CO_2(g) + 3\,H_2(g) \rightleftharpoons CH_3OH\,(g) + H_2O\,(g)}$$

$$\mathrm{CO_2(g) + H_2(g) \rightleftharpoons CO\,(g) + H_2O\,(g)}$$

Into a reactor maintained at 250 °C and 50 bar, a mixture containing $\mathrm{CO_2} : \mathrm{H_2}$ in a molar ratio of $1 : 4$ is fed. It has been found that the $\mathrm{CO_2}$ conversion is 30% and the $\mathrm{H_2}$ conversion is 18.5% when these two reactions are at equilibrium. No other processes need to be considered.

1.4 — 5 pt

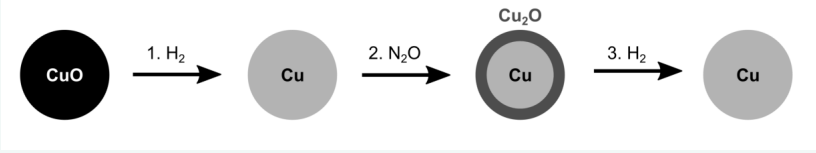
Calculate the thermodynamic equilibrium constants (at 250 °C) of the two reactions.

Heterogeneous copper-containing catalysts are commonly used for $\mathrm{CO_2}$ hydrogenation. Two specific, Cu-containing catalysts (A and B) showed promise for converting $\mathrm{CO_2}$ to methanol. These catalysts differ not only in their catalytic rates, but also in surface area, Cu content, and Cu dispersion (the ratio of surface Cu to the total Cu in the catalyst).

Cu dispersion is important, because only Cu species at the surface are active in $\mathrm{CO_2}$ hydrogenation. Under this assumption, 1 mole of active sites corresponds to 1 mole of surface Cu. The efficiency of these active sites is shown by their turnover frequencies (*TOF*, moles of product formed per moles of active site in a given time).

The **table** below reports the performance (reported as mass of produced methanol per total catalyst mass in a given time) and the specific surface areas of the two catalysts. The Cu content and dispersion of the catalysts was also measured and reported as follows:

1. At the start, all the copper in the catalysts (oxidized beforehand) is present as Cu(II); that was fully reduced to Cu(0) with hydrogen. No other species in the catalysts reacted with hydrogen besides copper oxides.
2. $\mathrm{N_2O}$ was introduced to the reduced samples at room temperature. At this temperature, $\mathrm{N_2O}$ only oxidizes active surface sites to Cu(I).
3. The Cu(I) active surface sites were reduced again to Cu(0) with hydrogen.



	Catalyst performance $(g_{MeOH}\, g_{cat}^{-1}\, h^{-1})$	Specific surface area $(m^2\, g_{cat}^{-1})$	H_2 consumed in step 1 $(mmol\, g_{cat}^{-1})$	H_2 consumed in step 3 $(mmol\, g_{cat}^{-1})$
Catalyst A	0.80	100	5.0	0.30
Catalyst B	0.90	120	4.0	0.70

1.5 — 3 pt

Find the methanol production rate per total mass of Cu (in $g_{MeOH}\, g_{Cu}^{-1}\, h^{-1}$) for catalysts A and B.

1.6 — 3 pt

Find the *TOF* (in h^{-1}) for catalysts A and B.

If you cannot find results, use $TOF_{\text{Catalyst } A} = 100\ h^{-1}$ *and* $TOF_{\text{Catalyst } B} = 1\ h^{-1}$ *in subsequent calculations.*

1.7 — 1 pt

Indicate the correct statement on the answer sheet.

a. Catalyst A has more efficient active sites.
b. Catalyst B has more efficient active sites.
c. The two catalysts have active sites with the same efficiency.

Avogadro constant:	$N_A = 6.022 \cdot 10^{23}\ mol^{-1}$	Gas constant:	$R = 8.314\ J\, mol^{-1}\, K^{-1}$
Ionic product of water at 298.15 K:	$K_w = 10^{-14}$	Zero of the Celsius scale:	$0\ °C = 273.15\ K$
Faraday constant:	$F = 96485\ C\, mol^{-1}$	Planck constant:	$h = 6.626 \cdot 10^{-34}\ J\, s$
Speed of light:	$c = 2.998 \cdot 10^{8}\ m\, s^{-1}$	Standard pressure:	$p^\circ = 1 \cdot 10^5\ Pa = 1\ bar$
Ideal gas law:	$pV = nRT$	Beer-Lambert law:	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon \cdot l \cdot c$
Enthalpy:	$H = U + pV$	Gibbs energy:	$G = H - TS$
$\Delta_r G^\circ = -RT \ln K = -nFE^\circ_{cell}$		Henderson-Hasselbalch equation:	$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$
Arrhenius equation:	$k = A \exp\left(-\frac{E_A}{RT}\right)$	Zeroth order integrated rate law:	$[A] = [A]_0 - kt$
Surface of a sphere:	$A = 4\pi R^2$	First order integrated rate law:	$\ln[A] = \ln[A]_0 - kt$
Volume of a sphere:	$V = \frac{4\pi}{3} R^3$	$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}$ for $\lvert r\rvert < 1$	

Periodic table

1												13	14	15	16	17	18
1 H 1.008	2											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	2 He 4.003
3 Li 6.94	4 Be 9.01											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Official English text of the problem.

Answers

- **1.1:** Nitrogen conversion $= 51.0\%$.
- **1.2:** $\mathrm{CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2}$; $m_{\mathrm{CO_2}} = 5.46\ \mathrm{kg} \approx 5.5\ \mathrm{kg}$ per $1.0\ \mathrm{kg}$ of hydrogen. The species are methane `C`, water `O`, carbon dioxide `O=C=O`, and hydrogen `[H][H]`.
- **1.3:** $m_{\mathrm{CO_2,\,blue}} = 9.74 \times 10^4\ \mathrm{kg} \approx 9.7 \times 10^4\ \mathrm{kg}$.
- **1.4:** Methanol synthesis: $K = 2.26 \times 10^{-5}$. Carbon monoxide formation: $K = 1.05 \times 10^{-2}$. Both are dimensionless and apply at $250\ ^\circ\mathrm{C}$.
- **1.5:** Catalyst A: 2.52; catalyst B: 3.54, in $\mathrm{g_{MeOH}\,g_{Cu}^{-1}\,h^{-1}}$, or 2.5 and 3.5 to two significant figures.
- **1.6:** $TOF_A = 41.6\ \mathrm{h^{-1}}$ and $TOF_B = 20.1\ \mathrm{h^{-1}}$, or 42 and $20\ \mathrm{h^{-1}}$ to two significant figures.
- **1.7: a. Catalyst A has more efficient active sites.**

Solution

The molecular species used in the solution have the following names and SMILES:

Formula	Name	SMILES
$\mathrm{N_2}$	Nitrogen	`N#N`
$\mathrm{H_2}$	Hydrogen	`[H][H]`
$\mathrm{NH_3}$	Ammonia	`N`
$\mathrm{CH_4}$	Methane	`C`
$\mathrm{H_2O}$	Water	`O`
CO	Carbon monoxide	`[C-]#[O+]`
$\mathrm{CO_2}$	Carbon dioxide	`O=C=O`
$\mathrm{CH_3OH}$	Methanol	`CO`
$\mathrm{N_2O}$	Nitrous oxide	`N#[N+][O-]`

Copper metal has the atomic SMILES `[Cu]`. Copper(II) oxide, CuO, and copper(I) oxide, $\mathrm{Cu_2O}$, can be encoded as formal ionic formula units `[Cu+2].[O-2]` and `[Cu+].[Cu+].[O-2]`, respectively. These solids are extended structures; the encodings do not specify their crystal lattices or surface coordination.

For the gas equilibria, use ideal-gas activities,

$$a_i = \frac{p_i}{p^\circ}, \qquad p^\circ = 1\ \mathrm{bar}.$$

This makes the thermodynamic equilibrium constants dimensionless.

1.1 — Equilibrium conversion of nitrogen

The balanced ammonia synthesis reaction is

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}.$$

From the supplied thermochemical data,

$$\Delta_r H^\circ = 2(-45.9) = -91.8\ \mathrm{kJ\,mol^{-1}},$$

and

$$\begin{aligned}\Delta_r S^\circ &= 2(192.8) - 191.6 - 3(130.7)\\ &= -198.1\ \mathrm{J\,mol^{-1}\,K^{-1}}.\end{aligned}$$

At $T = 400 + 273.15 = 673.15\ \mathrm{K}$,

$$\begin{aligned}\Delta_r G^\circ &= \Delta_r H^\circ - T\Delta_r S^\circ\\ &= -91800 - (673.15)(-198.1)\\ &= 41551\ \mathrm{J\,mol^{-1}}.\end{aligned}$$

Therefore,

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(-\frac{41551}{8.314(673.15)}\right) = 5.96535 \times 10^{-4}.$$

Take an initial mixture of $1\ \mathrm{mol}$ nitrogen and $3\ \mathrm{mol}$ hydrogen. Let x be the fraction of nitrogen converted.

Species	Initial amount / mol	Equilibrium amount / mol
$\mathrm{N_2}$	1	$1 - x$
$\mathrm{H_2}$	3	$3(1 - x)$
$\mathrm{NH_3}$	0	$2x$
Total	4	$4 - 2x$

Since $p_i = y_i P$,

$$\begin{aligned}K &= \frac{(p_{\mathrm{NH_3}}/p^\circ)^2}{(p_{\mathrm{N_2}}/p^\circ)(p_{\mathrm{H_2}}/p^\circ)^3}\\ &= \frac{4x^2(4-2x)^2}{27(1-x)^4}\left(\frac{p^\circ}{P}\right)^2.\end{aligned}$$

With $P/p^\circ = 100$, taking the positive square root gives

$$\frac{x(2-x)}{(1-x)^2} = \frac{\sqrt{27}}{4}(100)\sqrt{K} = 3.17278.$$

Using $x(2-x) = 1-(1-x)^2$,

$$\frac{1}{(1-x)^2} - 1 = 3.17278,$$

so the physically admissible root is

$$x = 1 - \frac{1}{\sqrt{4.17278}} = 0.510461.$$

Thus,

$$\boxed{\text{Nitrogen conversion} = 100x = 51.0\%.}$$

1.2 — Carbon dioxide from the combined reforming process

The two balanced steps are steam reforming,

$$\mathrm{CH_4 + H_2O \longrightarrow CO + 3\,H_2},$$

and the water–gas shift reaction,

$$\mathrm{CO + H_2O \longrightarrow CO_2 + H_2}.$$

Adding them and cancelling the intermediate carbon monoxide gives

$$\boxed{\mathrm{CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2}}.$$

The supplied atomic masses give

$$M_{\mathrm{H_2}} = 2(1.008) = 2.016\ \mathrm{g\,mol^{-1}},$$
$$M_{\mathrm{CO_2}} = 12.01 + 2(16.00) = 44.01\ \mathrm{g\,mol^{-1}}.$$

One mole of carbon dioxide accompanies four moles of hydrogen. Hence

$$\begin{aligned} m_{\mathrm{CO_2}} &= (1.0\ \mathrm{kg})\frac{44.01}{4(2.016)} \\ &= 5.4576\ \mathrm{kg}. \end{aligned}$$

Therefore,

$$\boxed{m_{\mathrm{CO_2}} \approx 5.5\ \mathrm{kg\ per\ 1.0\ kg\ of\ hydrogen}.}$$

1.3 — Carbon dioxide capture for blue ammonia

Use a single equilibrium pass of the stoichiometric feed. Both nitrogen and hydrogen have the same fractional conversion x, because they are supplied and consumed in the ratio $1:3$.

For each $2x$ mol of ammonia formed, the initial feed contains 3 mol of hydrogen. Therefore,

$$n_{\mathrm{H_2,\,feed}} = \frac{3}{2x} n_{\mathrm{NH_3}}.$$

The molar mass of ammonia is

$$M_{\mathrm{NH_3}} = 14.01 + 3(1.008) = 17.034\ \mathrm{g\,mol^{-1}}.$$

Thus,

$$\begin{aligned} m_{\mathrm{H_2,\,feed}} &= m_{\mathrm{NH_3}} \frac{3M_{\mathrm{H_2}}}{2xM_{\mathrm{NH_3}}} \\ &= (40000\ \mathrm{kg})\frac{3(2.016)}{2(0.510461)(17.034)} \\ &= 13911.1\ \mathrm{kg}. \end{aligned}$$

The real reforming process produces 7.0 kg of carbon dioxide per kilogram of hydrogen supplied. Consequently,

$$\begin{aligned} m_{\mathrm{CO_2,\,blue}} &= 7.0\, m_{\mathrm{H_2,\,feed}} \\ &= 97377.9\ \mathrm{kg}. \end{aligned}$$

All of this carbon dioxide must be captured:

$$\boxed{m_{\mathrm{CO_2,\,blue}} \approx 9.7 \times 10^4\ \mathrm{kg}.}$$

The conversion factor is needed because some of the supplied hydrogen remains unreacted at equilibrium.

1.4 — Equilibrium constants for methanol and carbon monoxide formation

The two reactions are methanol synthesis,

$$\mathrm{CO_2\,(g) + 3\,H_2\,(g) \rightleftharpoons CH_3OH\,(g) + H_2O\,(g)},$$

and the reverse water–gas shift reaction,

$$\mathrm{CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)}.$$

Take a feed containing 1.000 mol carbon dioxide and 4.000 mol hydrogen. Let ξ_{M} and ξ_{CO} be the reaction extents for methanol synthesis and carbon monoxide formation.

The carbon dioxide conversion gives

$$\xi_{\mathrm{M}} + \xi_{\mathrm{CO}} = 0.300\ \mathrm{mol}.$$

The hydrogen conversion gives

$$3\xi_{\mathrm{M}} + \xi_{\mathrm{CO}} = (0.185)(4.000) = 0.740\ \mathrm{mol}.$$

Subtracting,

$$2\xi_{\mathrm{M}} = 0.440\ \mathrm{mol},$$

so

$$\xi_{\mathrm{M}} = 0.220\ \mathrm{mol}, \qquad \xi_{\mathrm{CO}} = 0.080\ \mathrm{mol}.$$

The equilibrium composition and partial pressures at $P = 50\ \mathrm{bar}$ are:

Species	Equilibrium amount / mol	Partial pressure / bar
$\mathrm{CO_2}$	$1 - 0.220 - 0.080 = 0.700$	7.6754
$\mathrm{H_2}$	$4 - 3(0.220) - 0.080 = 3.260$	35.7456
$\mathrm{CH_3OH}$	0.220	2.4123
$\mathrm{H_2O}$	$0.220 + 0.080 = 0.300$	3.2895
CO	0.080	0.87719
Total	4.560	50.000

For methanol synthesis, $\Delta\nu = -2$. Therefore,

$$K_{\mathrm{M}} = \frac{a_{\mathrm{CH_3OH}} a_{\mathrm{H_2O}}}{a_{\mathrm{CO_2}} a_{\mathrm{H_2}}^{3}}.$$

Substituting $a_i = (n_i/n_{\mathrm{tot}})(P/p^{\circ})$,

$$\begin{aligned} K_{\mathrm{M}} &= \frac{(0.220)(0.300)(4.560)^2}{(0.700)(3.260)^3}\left(\frac{1}{50}\right)^2 \\ &= 2.26351 \times 10^{-5}. \end{aligned}$$

Thus,

$$\boxed{K_{\mathrm{M}} = 2.26 \times 10^{-5}.}$$

For carbon monoxide formation, $\Delta\nu = 0$, so total pressure and total amount cancel:

$$\begin{aligned} K_{\mathrm{CO}} &= \frac{a_{\mathrm{CO}} a_{\mathrm{H_2O}}}{a_{\mathrm{CO_2}} a_{\mathrm{H_2}}} \\ &= \frac{(0.080)(0.300)}{(0.700)(3.260)} \\ &= 0.0105171. \end{aligned}$$

Hence,

$$\boxed{K_{\mathrm{CO}} = 1.05 \times 10^{-2}.}$$

Both constants are dimensionless and correspond to $250\ ^{\circ}\mathrm{C} = 523.15\ \mathrm{K}$.

1.5 — Methanol production per total mass of copper

In step 1, copper(II) oxide is fully reduced:

$$\mathrm{CuO} + \mathrm{H_2} \longrightarrow \mathrm{Cu} + \mathrm{H_2O}.$$

One mole of hydrogen reduces one mole of copper. Thus,

$$n_{\mathrm{Cu,total}} = n_{\mathrm{H_2,\,step\ 1}}.$$

Using $M_{\mathrm{Cu}} = 63.55\ \mathrm{g\,mol^{-1}}$, the copper contents are

$$\begin{aligned} \left(\frac{m_{\mathrm{Cu}}}{m_{\mathrm{cat}}}\right)_A &= (5.0 \times 10^{-3})(63.55) = 0.31775\ \mathrm{g_{Cu}\,g_{cat}^{-1}}, \\ \left(\frac{m_{\mathrm{Cu}}}{m_{\mathrm{cat}}}\right)_B &= (4.0 \times 10^{-3})(63.55) = 0.25420\ \mathrm{g_{Cu}\,g_{cat}^{-1}}. \end{aligned}$$

Divide each reported production rate by its copper mass fraction:

$$\begin{aligned} r_{A,\mathrm{Cu}} &= \frac{0.80}{0.31775} = 2.5177\ \mathrm{g_{MeOH}\,g_{Cu}^{-1}\,h^{-1}}, \\ r_{B,\mathrm{Cu}} &= \frac{0.90}{0.25420} = 3.5405\ \mathrm{g_{MeOH}\,g_{Cu}^{-1}\,h^{-1}}. \end{aligned}$$

Therefore, to two significant figures,

$$\boxed{r_{A,\mathrm{Cu}} = 2.5, \qquad r_{B,\mathrm{Cu}} = 3.5 \quad \mathrm{g_{MeOH}\,g_{Cu}^{-1}\,h^{-1}}.}$$

1.6 — Turnover frequencies

The selective oxidation of surface copper in step 2 is

$$2\,\mathrm{Cu} + \mathrm{N_2O} \longrightarrow \mathrm{Cu_2O} + \mathrm{N_2}.$$

In step 3, the resulting copper(I) oxide is reduced:

$$\mathrm{Cu_2O + H_2 \longrightarrow 2\,Cu + H_2O}.$$

Thus, one mole of hydrogen consumed in step 3 corresponds to **two moles of surface copper**, and hence two moles of active sites:

$$n_{\text{sites}} = 2n_{\mathrm{H_2,\ step\ 3}}.$$

Per gram of catalyst,

$$n_{\text{sites},A} = 2(0.30) = 0.60\ \text{mmol}\,\text{g}_{\text{cat}}^{-1},$$
$$n_{\text{sites},B} = 2(0.70) = 1.40\ \text{mmol}\,\text{g}_{\text{cat}}^{-1}.$$

These correspond to copper dispersions of

$$D_A = \frac{0.60}{5.0} = 12\%, \qquad D_B = \frac{1.40}{4.0} = 35\%.$$

The molar mass of methanol is

$$M_{\mathrm{CH_3OH}} = 12.01 + 4(1.008) + 16.00 = 32.042\ \text{g}\,\text{mol}^{-1}.$$

By definition,

$$TOF = \frac{\text{moles of methanol produced per hour}}{\text{moles of active sites}}.$$

For catalyst A,

$$TOF_A = \frac{0.80/32.042}{0.60 \times 10^{-3}} = 41.612\ \text{h}^{-1}.$$

For catalyst B,

$$TOF_B = \frac{0.90/32.042}{1.40 \times 10^{-3}} = 20.063\ \text{h}^{-1}.$$

Therefore,

$$\boxed{TOF_A \approx 42\ \text{h}^{-1}, \qquad TOF_B \approx 20\ \text{h}^{-1}.}$$

The specific surface areas are unnecessary for this calculation because the hydrogen consumption directly measures the amount of active surface copper.

1.7 — Efficiency of the active sites

Active-site efficiency is measured by the turnover frequency. Here,

$$\frac{TOF_A}{TOF_B} = \frac{41.612}{20.063} \approx 2.07.$$

Each active site on catalyst A therefore produces approximately twice as much methanol per unit time as an active site on catalyst B.

Select:

$$\boxed{\text{a. Catalyst } A \text{ has more efficient active sites.}}$$

The solution was checked against the official solution.

Problem 2: Electronic nose

Resistive gas sensors, especially those using semiconducting metal oxides (SMOX), are becoming increasingly popular. They can detect tiny amounts of impurities, are small and stable, and are easy to make and use. These features make SMOX sensors stand out among the many types of gas sensors that work on different physical and chemical principles.

The mixed oxide **X** that has the normal spinel crystal structure, $\mathrm{A^{2+}B_2{}^{3+}O_4{}^{2-}}$, is an example of one of these SMOX materials. **X** can be obtained by decomposition of the crystalline hydrated metal oxalate $\mathrm{ZC_2O_4 \cdot \mathit{k}H_2O}$ of metal **Z** on air. When heated to $140\ ^\circ\mathrm{C}$, the crystalline hydrate loses 19.7% of its mass. Further heating in air leads to the formation of 2.407 g of black colored **X** at $500\ ^\circ\mathrm{C}$ and $3.8\ \mathrm{dm^3}$ of carbon dioxide at 101325 Pa.

2.1 Determine the formula of **X** and the value of k in $\mathrm{ZC_2O_4 \cdot \mathit{k}H_2O}$. **4 pt**

In the spinel structures oxygen atoms form a face centered cubic (FCC) lattice. In normal spinels the $\mathrm{A^{2+}}$ cations occupy part of the tetrahedral, and the $\mathrm{B^{3+}}$ cations occupy part of the octahedral lattice sites.

2.2 Calculate the percentage of the tetrahedral sites that is occupied in the case of a normal spinel $\mathrm{A^{2+}B_2{}^{3+}O_4{}^{2-}}$. **2 pt**

In addition to the normal spinels, the $\mathrm{MM'_2O_4}$ general formula also describes the inverse and the mixed spinel structures. Here M are the tetrahedrally coordinated, $\mathrm{M'}$ the octahedrally coordinated cations, but contrary to normal spinels, particular cations are not restricted to a single lattice site. A characteristic of the inverse spinel structures is that the electron configuration of the $\mathrm{M'}$ site cations is d^0, d^5 or d^{10}.

2.3 Select on the answer sheet two of the given formulas, which correspond to the structure of inverse spinel: $\mathrm{Fe_3O_4}$, $\mathrm{NiFe_2O_4}$, $\mathrm{Mn_3O_4}$, $\mathrm{FeCr_2O_4}$. **1 pt**

Semiconductors are materials whose orbitals contain a small excess or deficit of electrons, leading to negative or positive charges (holes), respectively. These charges can move through the semiconductor and allow it to conduct electricity. Chemical reactions can increase or decrease the charge on a semiconductor, altering its conductivity.

X is an example of a semiconductor where electricity is carried by positive charges (holes). For a resistive gas sensor based on **X**, the resistance R is measured over time t, while passing a gas over the sensor. This allows redox reactions to occur between the gas and the semiconductor surface, which will change the resistance of the sensor depending on the donor/acceptor properties of the gas. **Figure 1** shows the two different types of signal obtained this way.

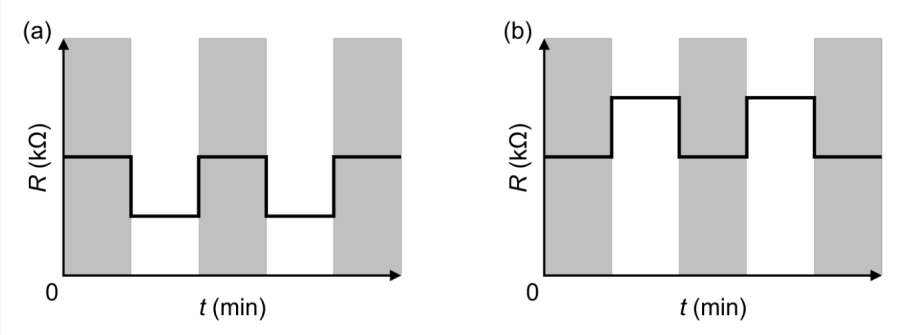


Figure 1: plot of resistance against time for two possible signal types, (a) and (b).

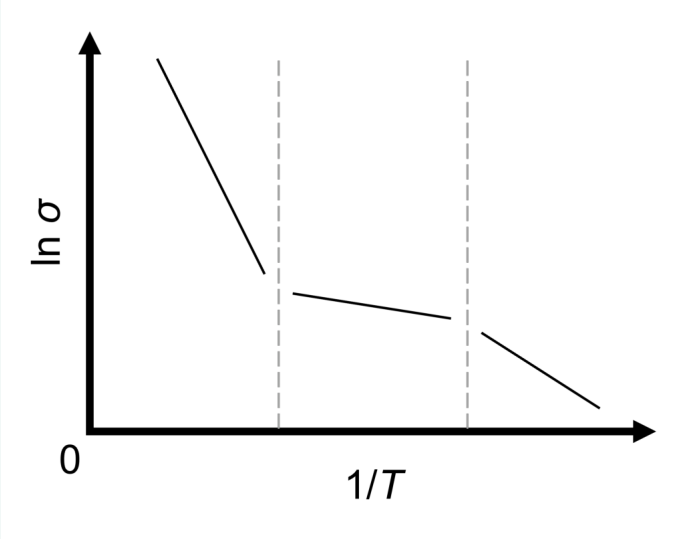
Grey bars = air, white bars = air + analyte gas.

2.4 Correlate the signal type (a or b) obtained from the **X** based sensor with the analyte gases ($\mathrm{H_2S}$, $\mathrm{O_3}$, $\mathrm{NO_2}$, $\mathrm{NH_3}$) during their detection at low concentrations. **2 pt**

The dependence of the specific conductivity (σ) of **X** on temperature is described by the Arrhenius law: $\sigma(T) = \sigma_0 \exp(-E_a/(RT))$, where E_a is the activation energy of conductivity. Three types of conductivity can be distinguished in different temperature ranges:

Ionization (I): 444–570 K, Impurity (II): 585–765 K, and Intrinsic (III): 800–905 K.

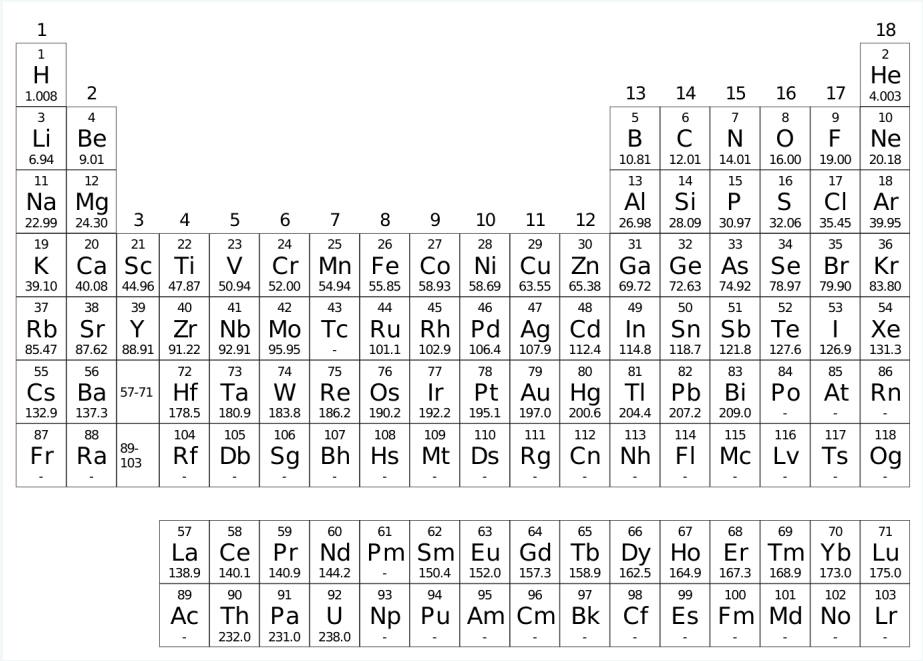
The sketch below illustrates the conductivity-temperature relation for the three temperature ranges.



2.5 Based on the sketch above, **order** the activation energies associated with the different conductivity types, $E_a(I)$, $E_a(II)$, and $E_a(III)$, from largest to smallest. **3 pt**

Avogadro constant:	$N_A = 6.022 \cdot 10^{23}\,\mathrm{mol^{-1}}$	Gas constant:	$R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Ionic product of water at 298.15 K:	$K_w = 10^{-14}$	Zero of the Celsius scale:	$0\,^\circ\mathrm{C} = 273.15\,\mathrm{K}$
Faraday constant:	$F = 96485\,\mathrm{C\,mol^{-1}}$	Planck constant:	$h = 6.626 \cdot 10^{-34}\,\mathrm{J\,s}$
Speed of light:	$c = 2.998 \cdot 10^{8}\,\mathrm{m\,s^{-1}}$	Standard pressure:	$p^\circ = 1 \cdot 10^5\,\mathrm{Pa} = 1\,\mathrm{bar}$
Ideal gas law:	$pV = nRT$	Beer-Lambert law:	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon \cdot l \cdot c$
Enthalpy:	$H = U + pV$	Gibbs energy:	$G = H - TS$
$\Delta_r G^\circ = -RT\ln K = -nFE^\circ_{\mathrm{cell}}$		Henderson-Hasselbalch equation:	$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right)$
Arrhenius equation:	$k = A\exp\left(-\frac{E_A}{RT}\right)$	Zeroth order integrated rate law:	$[\mathrm{A}] = [\mathrm{A}]_0 - kt$
Surface of a sphere:	$A = 4\pi R^2$	First order integrated rate law:	$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$
Volume of a sphere:	$V = \frac{4\pi}{3}R^3$	$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}$ for $\lvert r\rvert < 1$	

Periodic table



Official English text of the problem.

Answers

- **2.1:** $\boxed{X = \mathrm{Co_3O_4}, \quad k = 2}$. **X** is cobalt(II,III) oxide; the precursor is cobalt(II) oxalate dihydrate, $\mathrm{CoC_2O_4 \cdot 2\,H_2O}$.
- **2.2:** $\boxed{12.5\%}$ of the tetrahedral sites.
- **2.3:** $\boxed{\mathrm{Fe_3O_4}}$ and $\boxed{\mathrm{NiFe_2O_4}}$: magnetite and nickel(II) ferrite.
- **2.4:** **(a)** ozone, $\mathrm{O_3}$, `[O-][O+]=O`, and nitrogen dioxide, $\mathrm{NO_2}$, `[O-][N+]=O`; **(b)** hydrogen sulfide, $\mathrm{H_2S}$, `S`, and ammonia, $\mathrm{NH_3}$, `N`.
- **2.5:** $\boxed{E_a(\mathrm{III}) > E_a(\mathrm{I}) > E_a(\mathrm{II})}$.

Solution

2.1 — Identification of the oxide and hydrate

Because the precursor contains only one metal, the spinel must contain that metal in two oxidation states and have the formula $\mathrm{Z_3O_4}$. The overall oxidation of the anhydrous oxalate in air is

$$3\,\mathrm{ZC_2O_4} + 2\,\mathrm{O_2} \longrightarrow \mathrm{Z_3O_4} + 6\,\mathrm{CO_2}.$$

Consequently,

$$n(\mathrm{Z_3O_4}) = \frac{n(\mathrm{CO_2})}{6}.$$

Taking the gas temperature to be the stated decomposition temperature,

$$T = 500 + 273.15 = 773.15\,\mathrm{K}, \qquad V = 3.8 \times 10^{-3}\,\mathrm{m^3}.$$

The ideal gas law gives, retaining guard digits,

$$\begin{aligned} n(\mathrm{CO_2}) &= \frac{pV}{RT} \\ &= \frac{(101325\,\mathrm{Pa})(3.8 \times 10^{-3}\,\mathrm{m^3})}{(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})(773.15\,\mathrm{K})} \\ &= 0.0598999\ldots\ \mathrm{mol} \approx 0.060\,\mathrm{mol}. \end{aligned}$$

Thus the metal's molar mass is

$$\begin{aligned} M(\mathrm{Z}) &= \frac{M(\mathrm{Z_3O_4}) - 4M(\mathrm{O})}{3} \\ &= \frac{1}{3}\left[\frac{6(2.407\,\mathrm{g})}{0.0598999\ldots\ \mathrm{mol}} - 4(16.00\,\mathrm{g\,mol^{-1}})\right] \\ &\approx 59\,\mathrm{g\,mol^{-1}}. \end{aligned}$$

This is consistent with cobalt, whose supplied molar mass is $58.93\,\mathrm{g\,mol^{-1}}$, and its black normal-spinel oxide, cobalt(II,III) oxide:

$$\boxed{\mathrm{X = Co_3O_4}}.$$

Its molar mass is

$$M(\mathrm{Co_3O_4}) = 3(58.93) + 4(16.00) = 240.79\,\mathrm{g\,mol^{-1}}.$$

In the normal spinel, cobalt(II) ions, $\mathrm{Co^{2+}}$, `[Co+2]`, occupy tetrahedral sites; cobalt(III) ions, $\mathrm{Co^{3+}}$, `[Co+3]`, occupy octahedral sites. The anion lattice consists of oxide ions, $\mathrm{O^{2-}}$, `[O-2]`. These isolated-ion SMILES do not encode the extended crystal lattice or its coordination geometries.

The mass lost at $140\,^\circ\mathrm{C}$ is the water of crystallization. Using

$$M(\mathrm{CoC_2O_4}) = 58.93 + 2(12.01) + 4(16.00) = 146.95\,\mathrm{g\,mol^{-1}}$$

and $M(\mathrm{H_2O}) = 18.016\,\mathrm{g\,mol^{-1}}$,

$$\frac{18.016k}{146.95 + 18.016k} = 0.197.$$

Therefore,

$$k = \frac{0.197(146.95)}{(1-0.197)(18.016)} = 2.001\ldots,$$

so

$$\boxed{k = 2}.$$

The balanced steps are

$$\mathrm{CoC_2O_4 \cdot 2\,H_2O\,(s) \longrightarrow CoC_2O_4\,(s) + 2\,H_2O\,(g)} \qquad (140\,^\circ\mathrm{C})$$

and

$$\mathrm{3\,CoC_2O_4\,(s) + 2\,O_2\,(g) \longrightarrow Co_3O_4\,(s) + 6\,CO_2\,(g)} \qquad (500\,^\circ\mathrm{C}).$$

For the dihydrate, the calculated water content is

$$\frac{2(18.016)}{146.95 + 2(18.016)} \times 100\% = 19.69\ldots\% \approx 19.7\%.$$

The molecular species in these equations are water `O`, dioxygen `O=O`, and carbon dioxide `O=C=O`. The oxalate ion, $\mathrm{C_2O_4^{2-}}$, has SMILES `[O-]C(=O)C(=O)[O-]`. A composition-only ionic SMILES for cobalt(II) oxalate dihydrate is `[Co+2].[O-]C(=O)C(=O)[O-].O.O`; it does not specify the solid's coordination structure. The dioxygen SMILES does not specify its triplet ground state.

2.2 — Occupancy of tetrahedral sites

An FCC array containing N oxide ions has $2N$ tetrahedral holes.

Each formula unit of a normal spinel contains four oxide ions, corresponding to

$$2 \times 4 = 8$$

tetrahedral holes. Only its one $\mathrm{A^{2+}}$ cation occupies a tetrahedral hole; the two $\mathrm{B^{3+}}$ cations occupy octahedral holes.

Hence,

$$\boxed{\text{Tetrahedral-site occupancy} = \frac{1}{8} \times 100\% = 12.5\%.}$$

2.3 — Selection of inverse spinels

A normal spinel places the divalent cation on tetrahedral sites and the trivalent cations on octahedral sites. An inverse spinel instead has the distribution

$$(\mathrm{B^{3+}})_{\mathrm{tet}}[\mathrm{A^{2+}B^{3+}}]_{\mathrm{oct}}\mathrm{O_4}.$$

The relevant ion identities are iron(II) `[Fe+2]`, iron(III) `[Fe+3]`, nickel(II) `[Ni+2]`, manganese(II) `[Mn+2]`, manganese(III) `[Mn+3]`, and chromium(III) `[Cr+3]`.

Their distributions in the four candidate oxides are:

Oxide	Tetrahedral cations per formula unit	Octahedral cations per formula unit	Type
$\mathrm{Fe_3O_4}$, iron(II,III) oxide (magnetite)	$\mathrm{Fe^{3+}}$, d^5	$\mathrm{Fe^{2+}}$, d^6, and $\mathrm{Fe^{3+}}$, d^5	**Inverse**
$\mathrm{NiFe_2O_4}$, nickel(II) ferrite	$\mathrm{Fe^{3+}}$, d^5	$\mathrm{Ni^{2+}}$, d^8, and $\mathrm{Fe^{3+}}$, d^5	**Inverse**
$\mathrm{Mn_3O_4}$, manganese(II,III) oxide	$\mathrm{Mn^{2+}}$, d^5	Two $\mathrm{Mn^{3+}}$, each d^4	Normal
$\mathrm{FeCr_2O_4}$, iron(II) chromite	$\mathrm{Fe^{2+}}$, d^6	Two $\mathrm{Cr^{3+}}$, each d^3	Normal

High-spin $\mathrm{Fe^{3+}}$, with configuration d^5, has zero crystal-field stabilization energy in either tetrahedral or octahedral coordination. The octahedral preferences of $\mathrm{Fe^{2+}}$ and especially $\mathrm{Ni^{2+}}$ therefore favor the inverse arrangements of the two ferrites.

For the other candidates, $\mathrm{Mn^{3+}}$ and $\mathrm{Cr^{3+}}$ favor octahedral coordination, supporting normal arrangements.

The two formulas to select are therefore

$$\boxed{\mathrm{Fe_3O_4} \quad \text{and} \quad \mathrm{NiFe_2O_4}}.$$

The statement's criterion that the $\mathrm{M'}$ (octahedral) cations of an inverse spinel are d^0, d^5 or d^{10} appears to contain a site-label error: in both selected inverse spinels the octahedral sites hold d^6 $\mathrm{Fe^{2+}}$ or d^8 $\mathrm{Ni^{2+}}$ alongside d^5 $\mathrm{Fe^{3+}}$, while the tetrahedral sites hold only d^5 $\mathrm{Fe^{3+}}$.

2.4 — Gas response of the sensor

The oxide is a **p-type semiconductor**: its mobile charge carriers are holes.

An electron-accepting, oxidizing gas removes electrons from the semiconductor surface, increasing the hole concentration. Conductivity increases and resistance decreases, giving **signal (a)** during the white intervals.

An electron-donating, reducing gas supplies electrons that recombine with holes. Conductivity decreases and resistance increases, giving **signal (b)**.

Analyte	Redox behavior	Effect on hole concentration	Resistance during exposure	Signal
Hydrogen sulfide, $\mathrm{H_2S}$, `S`	Reducing; electron donor	Decreases	Increases	**b**
Ozone, $\mathrm{O_3}$, `[O-][O+]=O`	Oxidizing; electron acceptor	Increases	Decreases	**a**
Nitrogen dioxide, $\mathrm{NO_2}$, `[O-][N+]=O`	Oxidizing; electron acceptor	Increases	Decreases	**a**
Ammonia, $\mathrm{NH_3}$, `N`	Reducing; electron donor	Decreases	Increases	**b**

The ozone and nitrogen dioxide SMILES show individual resonance representations. Both molecules are bent, and nitrogen dioxide is a radical. The surface electron transfer and resulting changes in carrier concentration are described above; molecular SMILES alone do not show them.

2.5 — Ordering the activation energies

Taking logarithms of the Arrhenius expression,

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{R}\frac{1}{T}.$$

Thus the slope of a plot of $\ln \sigma$ against $1/T$ is

$$\boxed{\text{slope} = -\frac{E_a}{R}}.$$

A larger magnitude of negative slope corresponds to a larger activation energy.

Because the horizontal coordinate is $1/T$, temperature decreases from left to right. The three segments therefore represent:

Position on the graph	Temperature range	Conductivity type	Magnitude of slope
Left	800–905 K	Intrinsic, III	Largest
Middle	585–765 K	Impurity, II	Smallest
Right	444–570 K	Ionization, I	Intermediate

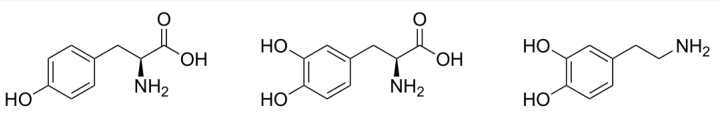
Hence,

$$\boxed{E_a(\mathrm{III}) > E_a(\mathrm{I}) > E_a(\mathrm{II})}.$$

The solution was checked against the official solution.

Problem 3: Tyrosinase

The enzyme tyrosine 3-monooxygenase has an important biological role because it catalyzes the initial and rate-limiting step in the biosynthesis of the neurotransmitter dopamine. In this first step, L-DOPA is produced from the amino acid L-tyrosine (Tyr) in the presence of dissolved oxygen, tetrahydrofolic acid and ferrous ions. In a subsequent step, another enzyme transforms L-DOPA into dopamine.



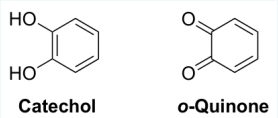
L-Tyrosine **L-DOPA** **Dopamine**

The activity of the tyrosine 3-monooxygenase enzyme is described well by the simplest model of enzyme action, the Michaelis-Menten equation. This gives the rate of the formation (r) of L-DOPA as a function of the enzyme (E) and substrate Tyr (S) concentrations as follows:

$$r = \frac{k[E][S]}{K_\mathrm{M} + [S]}$$

The following values of enzymatic turnover frequency ($k = 250\ \mathrm{min^{-1}}$) and Michaelis constant ($K_\mathrm{M} = 0.49\ \mathrm{mmol\,dm^{-3}}$) can be used in this task when needed.

Catechol (1,2-dihydroxybenzene) inactivates the enzyme tyrosine 3-monooxygenase irreversibly by turning it into an inactive form. When a carefully purified sample of catechol is mixed with the enzyme with the exclusion of dissolved oxygen, no change is seen at all. So the reaction of catechol with dissolved oxygen, which produces *o*-quinone, must be important.



Catechol ***o*-Quinone**

This process can be studied in the absence of the enzyme. A test experiment in a reactor not in contact with ambient air at $37\ ^\circ\mathrm{C}$ and at pH 7.5 gave the following kinetic data:

time (min)	catechol concentration ($\mathrm{mmol\,dm^{-3}}$)	oxygen concentration ($\mathrm{mmol\,dm^{-3}}$)	*o*-quinone concentration ($\mu\mathrm{mol\,dm^{-3}}$)
0	2.00	0.200	0
20.0	1.97	0.170	30
40.0	1.94	0.140	60
60.0	1.91	0.111	89
80.0	1.88	0.083	117

time (min)	catechol concentration ($\mathrm{mmol\,dm^{-3}}$)	oxygen concentration ($\mathrm{mmol\,dm^{-3}}$)	*o*-quinone concentration ($\mu\mathrm{mol\,dm^{-3}}$)
100.0	1.85	0.054	146

3.1 — 5.0 pt

Identify the only by-product (which is not one of the molecules shown in the table above) and **write** the balanced equation of the process with molecular formulas based on the kinetic data.

3.2 — 2.0 pt

Calculate the initial rate (r_0) of *o*-quinone formation in this experiment with an appropriate unit.

The rate law of the process was determined by varying the initial concentrations of the reactants. Changing the oxygen concentration did not influence the initial rate of the process. Using different catechol concentrations gave the following initial rates for *o*-quinone formation:

catechol concentration ($\mathrm{mmol\,dm^{-3}}$)	initial rate of *o*-quinone formation ($\mu\mathrm{mol\,dm^{-3}\,min^{-1}}$)
1.0	0.75
4.0	3.0
6.0	4.5
8.0	6.0
10.0	7.5

3.3 — 5.0 pt

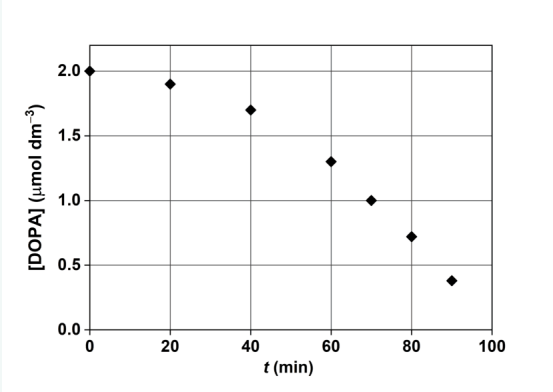
Determine the rate law of the reaction between catechol and oxygen producing *o*-quinone. **Calculate** the rate constant of this process (k_{catechol}) with an appropriate unit.

In separate experiments, it was confirmed that neither *o*-quinone, nor the by-product inactivates the enzyme alone, nor even in combination.

An experiment in which the enzyme is reacted with catechol in the presence of dissolved oxygen did show inactivation, though.

The experiment was done in an open vessel so that any oxygen consumed in the process could be continuously replenished from air. The initial concentration of the enzyme was $4.2\ \mathrm{nmol\,dm^{-3}}$, the initial concentration of catechol was $2.00\ \mathrm{mmol\,dm^{-3}}$ at $37\ ^\circ\mathrm{C}$ and at pH 7.5.

Samples were taken regularly from the enzyme-catechol reaction mixture, and the activity of the enzyme was assayed by adding L-tyrosine, tetrahydrofolic acid and ferrous ions. During the enzyme activity measurements, the concentration of added L-tyrosine was $10.0\ \mathrm{mmol\,dm^{-3}}$ and the concentration of L-DOPA in each assay sample was measured after 2.0 minutes. The following results were obtained:



inactivation reaction time t (min)	L-DOPA concentration after 2.0 minutes from the start of the assay $[\mathrm{DOPA}]$ ($\mu\mathrm{mol\,dm^{-3}}$)
0	2.0
20.0	1.9
40.0	1.7
60.0	1.3
70.0	1.00
80.0	0.72
90.0	0.38

3.4 — 4.0 pt

Derive a formula that allows you to calculate the actual concentration of active enzyme ($[E]$) from the data of these experiments in terms of k ($= 250\ \mathrm{min^{-1}}$), K_{M} ($= 0.49\ \mathrm{mmol\,dm^{-3}}$), and/or reagent concentrations.

The change in the active enzyme concentration as a function of time is well described by a parabola ($[E] = [E]_0 - k_{\mathrm{obs}}t^2$), where k_{obs} is an observed rate constant (i.e. one that can be written later as a combination of elementary rate constants and initial concentrations), and $[E]_0$ is the initial concentration of the enzyme.

3.5 — 3.0 pt

Give the value of k_{obs} with an appropriate unit.

3.6 — 3.0 pt

Determine the first half-life of the enzyme inactivation reaction. **Derive** a formula that gives the first half-life as a function of the initial enzyme concentration and of k_{obs}.

The first half-lives for enzyme inactivation were determined using other initial catechol concentrations. The dependences of active enzyme concentrations on time were very well described by parabolas in these cases as well.

catechol concentration ($\mathrm{mmol\,dm^{-3}}$)	first half-life (min)
1.0	140
4.0	35
6.0	23
8.0	17.5
10.0	14

3.7 — 6.0 pt

Derive a rate equation of the enzyme inactivation process consistent with all the experimental observations.

3.8 — 3.0 pt

What are the reactants of the rate determining step for the enzyme inactivation process? **Select** the ONLY correct option on the answer sheet.

A) catechol $+\ \mathrm{O_2} \longrightarrow \ldots$
B) catechol + o-quinone $\longrightarrow \ldots$
C) o-quinone $+\ \mathrm{O_2} \longrightarrow \ldots$
D) enzyme $+\ 2$ catechol $\longrightarrow \ldots$
E) enzyme $+\ \mathrm{O_2} \longrightarrow \ldots$
F) 2 catechol $+\ \mathrm{O_2} \longrightarrow \ldots$
G) enzyme + catechol $\longrightarrow \ldots$
H) enzyme + by-product $\longrightarrow \ldots$

Official English text of the problem.

Answers

- **3.1:** Hydrogen peroxide, $\mathrm{H_2O_2}$, SMILES `OO`.

$$\boxed{\mathrm{C_6H_6O_2 + O_2 \longrightarrow C_6H_4O_2 + H_2O_2}}$$

- **3.2:** $\boxed{r_0 = 1.5\ \mu\mathrm{mol\,dm^{-3}\,min^{-1}}}$.
- **3.3:** $\boxed{r = k_{\mathrm{catechol}}[\mathrm{catechol}]}$, first order in catechol and zero order in oxygen over the investigated range, with

$$\boxed{k_{\mathrm{catechol}} = 7.5 \times 10^{-4}\ \mathrm{min^{-1}}}.$$

- **3.4:** For assay duration $\tau = 2.0\ \mathrm{min}$,

$$\boxed{[E] = \frac{[\mathrm{DOPA}](K_{\mathrm{M}} + [S])}{k\tau[S]}}.$$

- **3.5:**

$$\boxed{k_{\mathrm{obs}} \approx 4.2 \times 10^{-4}\ \mathrm{nmol\,dm^{-3}\,min^{-2}} = 4.2 \times 10^{-13}\ \mathrm{mol\,dm^{-3}\,min^{-2}}}.$$

- **3.6:** Approximately $70\ \mathrm{min}$, with

$$\boxed{t_{1/2} = \sqrt{\frac{[E]_0}{2k_{\mathrm{obs}}}}}.$$

- **3.7:** Writing $C = [\mathrm{catechol}]$, $Q = [o\text{-quinone}]$, and $C_0 = C(0)$, a consistent rate equation is

$$\boxed{-\frac{d[E]}{dt} = k_I C Q \simeq k_I k_{\mathrm{catechol}} C_0^2 t}, \qquad \boxed{k_{\mathrm{obs}} = \frac{1}{2} k_I k_{\mathrm{catechol}} C_0^2}.$$

- **3.8: B — catechol + *o*-quinone.** Catechol: `Oc1ccccc1O`; *o*-quinone: `O=C1C=CC=CC1=O`.

Solution

3.1 — Identification of the by-product and balanced reaction

The relevant molecules are catechol (benzene-1,2-diol), `Oc1ccccc1O`, with formula $\mathrm{C_6H_6O_2}$; dioxygen, `O=O`; and *o*-quinone (1,2-benzoquinone), `O=C1C=CC=CC1=O`, with formula $\mathrm{C_6H_4O_2}$.

During the first $20.0\ \mathrm{min}$,

$$-\Delta[\mathrm{catechol}] = 2.00 - 1.97 = 0.030\ \mathrm{mmol\,dm^{-3}},$$
$$-\Delta[\mathrm{O_2}] = 0.200 - 0.170 = 0.030\ \mathrm{mmol\,dm^{-3}},$$

and

$$\Delta[o\text{-quinone}] = 30\ \mu\mathrm{mol\,dm^{-3}} = 0.030\ \mathrm{mmol\,dm^{-3}}.$$

Thus catechol consumption, oxygen consumption, and quinone formation occur in a $1:1:1$ molar ratio.

Converting one molecule of catechol into one molecule of quinone removes two hydrogen atoms. With one molecule of oxygen consumed, atom balance requires the remaining product to be hydrogen peroxide, $\mathrm{H_2O_2}$, oo:

$$\boxed{\mathrm{C_6H_6O_2 + O_2 \longrightarrow C_6H_4O_2 + H_2O_2}}.$$

Both sides contain six carbon atoms, six hydrogen atoms, and four oxygen atoms.

3.2 — Initial rate of quinone formation

The first interval gives the initial slope:

$$r_0 \simeq \frac{[\text{quinone}]_{20} - [\text{quinone}]_0}{20.0 - 0} = \frac{30 - 0}{20.0}.$$

Therefore,

$$\boxed{r_0 = 1.5\ \mu\mathrm{mol\,dm^{-3}\,min^{-1}}}.$$

The next interval gives the same slope to the precision of the data.

3.3 — Rate law and catechol oxidation rate constant

Write the empirical rate law as

$$r = k_{\text{catechol}}[\text{catechol}]^a[\mathrm{O_2}]^b.$$

Changing the oxygen concentration does not change the initial rate, so $b = 0$ over the investigated concentration range.

Increasing catechol concentration from 1.0 to $4.0\ \mathrm{mmol\,dm^{-3}}$ increases the rate from 0.75 to $3.0\ \mu\mathrm{mol\,dm^{-3}\,min^{-1}}$, also by a factor of four. All the other measurements show the same proportionality. Hence $a = 1$, and

$$\boxed{r = k_{\text{catechol}}[\text{catechol}]}.$$

Converting the numerator and denominator to matching concentration units,

$$k_{\text{catechol}} = \frac{0.75 \times 10^{-3}\ \mathrm{mmol\,dm^{-3}\,min^{-1}}}{1.0\ \mathrm{mmol\,dm^{-3}}} = \boxed{7.5 \times 10^{-4}\ \mathrm{min^{-1}}}.$$

The zero order in oxygen applies while oxygen is available under the experimental conditions; it does not imply that oxidation can proceed without oxygen.

3.4 — Active-enzyme concentration from the assay

The assay substrate is L-tyrosine, `N[C@@H](Cc1ccc(O)cc1)C(=O)O`, and its measured product is L-DOPA, `N[C@@H](Cc1ccc(O)c(O)c1)C(=O)O`. These SMILES represent the neutral structures shown in the paper, with the S configuration of both L-amino acids.

Let $\tau = 2.0\ \mathrm{min}$ denote the assay duration, distinct from the inactivation time t. The maximum product concentration is only $2.0\ \mu\mathrm{mol\,dm^{-3}}$, compared with $10.0\ \mathrm{mmol\,dm^{-3}}$ of substrate. Thus substrate depletion is at most

$$\frac{2.0 \times 10^{-3}}{10.0} \times 100\% = 0.020\%,$$

and $[S]$ can be treated as constant.

Under the short-assay approximation that the sampled active-enzyme concentration remains effectively constant,

$$\frac{[\mathrm{DOPA}]}{\tau} = r = \frac{k[E][S]}{K_\mathrm{M} + [S]}.$$

Rearranging gives

$$\boxed{[E] = \frac{[\mathrm{DOPA}]}{k\tau}\left(1 + \frac{K_\mathrm{M}}{[S]}\right)}.$$

Numerically,

$$[E] = [\mathrm{DOPA}]\frac{0.49 + 10.0}{250(2.0)(10.0)} = 0.002098[\mathrm{DOPA}],$$

when both concentrations use the same units. Equivalently,

$$\boxed{\frac{[E]}{\mathrm{nmol\,dm^{-3}}} = 2.098\ \frac{[\mathrm{DOPA}]}{\mu\mathrm{mol\,dm^{-3}}}}.$$

For the initial sample, this gives $2.098(2.0) = 4.196\ \mathrm{nmol\,dm^{-3}}$, agreeing with the stated $4.2\ \mathrm{nmol\,dm^{-3}}$.

3.5 — Observed rate constant

From

$$[E] = [E]_0 - k_{\text{obs}}t^2,$$

we obtain

$$k_{\text{obs}} = \frac{[E]_0 - [E](t)}{t^2}.$$

At $t = 90.0\ \mathrm{min}$,

$$[E](90) = 2.098(0.38) = 0.79724\ \mathrm{nmol\,dm^{-3}}.$$

Therefore,

$$k_{\mathrm{obs}} = \frac{4.2 - 0.79724}{(90.0)^2} = 4.2009 \times 10^{-4}\ \mathrm{nmol\,dm^{-3}\,min^{-2}}.$$

To sensible precision,

$$\boxed{k_{\mathrm{obs}} \approx 4.2 \times 10^{-4}\ \mathrm{nmol\,dm^{-3}\,min^{-2}}}.$$

A fit using all the measurements gives approximately 4.20×10^{-4} in the same units. Its units are concentration divided by time squared, as required by the parabolic equation.

3.6 — First half-life

The measured DOPA concentration is proportional to active-enzyme concentration. It falls from 2.0 to $1.00\ \mu\mathrm{mol\,dm^{-3}}$ at $t = 70.0\ \mathrm{min}$, so the experimental first half-life is approximately

$$\boxed{t_{1/2} \approx 70\ \mathrm{min}}.$$

In general, substituting $[E](t_{1/2}) = [E]_0/2$ gives

$$\frac{[E]_0}{2} = [E]_0 - k_{\mathrm{obs}} t_{1/2}^2.$$

Thus,

$$\boxed{t_{1/2} = \sqrt{\frac{[E]_0}{2k_{\mathrm{obs}}}}}.$$

Using the coefficient from 3.5 gives

$$t_{1/2} = \sqrt{\frac{4.2}{2(4.2 \times 10^{-4})}} = 70.7\ \mathrm{min},$$

consistent with about $70\ \mathrm{min}$ from the rounded experimental data.

3.7 — Rate equation for enzyme inactivation

Let

$$C = [\text{catechol}], \qquad Q = [o\text{-quinone}], \qquad C_0 = C(0).$$

First, differentiating the observed parabola gives

$$r_I \equiv -\frac{d[E]}{dt} = 2k_{\mathrm{obs}} t.$$

Thus the enzyme-loss rate increases approximately linearly with time.

Next, the half-life data show that

$$C_0 t_{1/2} \approx 140\ \mathrm{mmol\,dm^{-3}\,min}.$$

For example, $1.0(140) = 4.0(35) = 8.0(17.5) = 10.0(14) = 140$; the 6.0 entry gives 138, consistent with rounding. Therefore,

$$t_{1/2} \propto C_0^{-1}.$$

At the fixed initial enzyme concentration, the relation from 3.6 then requires

$$k_{\mathrm{obs}} \propto t_{1/2}^{-2} \propto C_0^2.$$

Writing $k_{\mathrm{obs}} = aC_0^2$, the directly inferred time-dependent rate equation is

$$\boxed{r_I = 2aC_0^2 t}.$$

To express this in terms of reacting species, use quinone formation:

$$\frac{dQ}{dt} = k_{\mathrm{catechol}} C.$$

For the approximate parabolic model, take $C \simeq C_0$. This is reasonable over the reported experiment: independent catechol oxidation changes its concentration by only about 6.5% in $90\ \mathrm{min}$. With initially negligible quinone,

$$Q(t) \simeq k_{\mathrm{catechol}} C_0 t.$$

A rate law first order in both catechol and quinone therefore gives

$$r_I = k_I C Q \simeq k_I k_{\mathrm{catechol}} C_0^2 t,$$

which has exactly the required time and initial-catechol dependences. Consequently, a consistent rate equation is

$$\boxed{-\frac{d[E]}{dt} = k_I [\text{catechol}][o\text{-quinone}]}.$$

Integrating under the same approximations,

$$\boxed{[E](t) \simeq [E]_0 - \frac{1}{2} k_I k_{\mathrm{catechol}} C_0^2 t^2},$$

so that

$$\boxed{k_{\text{obs}} = \frac{1}{2} k_I k_{\text{catechol}} C_0^2}.$$

Here k_I is defined for the rate of active-enzyme loss, including any fixed yield of inactivation per slow reaction event. Its fitted value is

$$k_I = \frac{2(4.2 \times 10^{-13})}{(7.5 \times 10^{-4})(2.00 \times 10^{-3})^2} \approx 2.8 \times 10^{-4}\ \text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1}.$$

This model accounts for the observations through slow generation of an inactivating species from catechol and quinone, followed by rapid reaction with the enzyme. Oxygen is needed to generate quinone; quinone and hydrogen peroxide without catechol do not provide this route. The enzyme concentration does not appear in the limiting rate while sufficient active enzyme remains to capture the generated species.

3.8 — Reactants of the rate-determining step

The rate law derived above is proportional to catechol concentration multiplied by quinone concentration. The corresponding listed reactants are therefore

$$\boxed{\text{B: catechol + } o\text{-quinone}}.$$

Catechol is `Oc1ccccc1O`, and *o*-quinone is `O=C1C=CC=CC1=O`.

Quinone accumulates approximately linearly with time, so its slow reaction with the nearly constant catechol concentration generates the inactivating species at an increasing rate. This produces the observed quadratic loss of active enzyme.

The solution was checked against the official solution.

Problem 4: Potassium

Elementary potassium was the first metal synthesized by electrolysis (1807). Humphry Davy used voltaic cells and electrodes immersed into molten KOH.

4.1 Give balanced equations for the processes taking place on the cathode (1) and the anode (2). **2 pt**

It is little known that only a year after Davy, French chemists have produced potassium in a chemical reduction. One of the methods involved a mixture of potassium carbonate and finely powdered carbon. This mixture was heated to very high temperatures in a gun barrel. Carbon monoxide and potassium vapors were leaving the end of the barrel, where the metal could be condensed to a solid.

4.2 Write down the balanced equation for the reaction giving only these two products. **1 pt**

The chemical production of potassium had a low yield. Depending on the circumstances, a considerable amount of reddish paste was left behind in the gun barrel. Gmelin isolated an interesting compound (**X**) from this residue in 1825 by recrystallization in water. The exact structure of the byproduct **X** was determined more than one and a half century later.

X is a hydrated salt (2 mol water : 1 mol of salt) forming golden yellow crystals. Its anion has an exceptionally symmetric (shown by vibrational spectra) and stable planar cyclic structure.

The diprotic acid (**Y**) that can be formed from the salt **X** has surprisingly (at least to the superficial observer) low $\text{p}K_a$ values: 0.8 and 2.2.

4.3 Give the pH where 95% of all dissolved acid **Y** is in the neutral acid form. **3 pt**

4.4 Calculate the pH of a $0.01\ \text{mol}\,\text{dm}^{-3}$ solution of the salt **X** in pure water. **4 pt**

The key step in the structure identification of **X** was the treatment of the anhydrous salt with methyl iodide. The salt reacted with two equivalents of methyl iodide. The somewhat volatile compound that was obtained had a molar mass of $170.12\ \text{g/mol}$ (measured in a mass spectrometer).

A number of analogous salts were also identified in the mixture in smaller quantities. The appropriate potassium salts when treated with two equivalent of MeI gave derivatives with molar masses of: $142.11\ \text{g/mol}$, $114.10\ \text{g/mol}$, $198.13\ \text{g/mol}$.

4.5 Give the empirical formula of Gmelin's compound **X**. **4 pt**

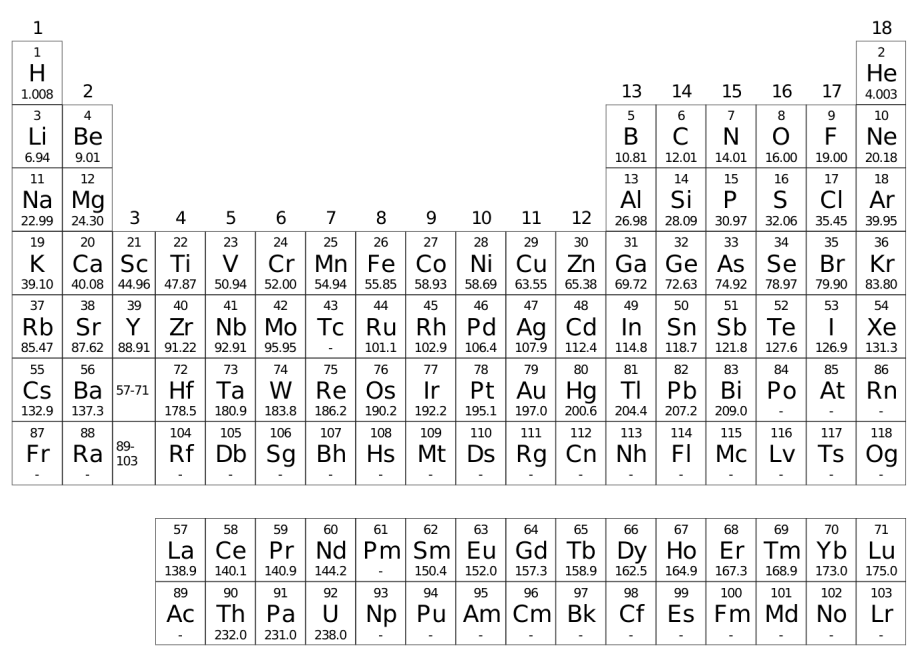
4.6 Draw the structure of the free acid **Y**. **3 pt**

The extraordinary stability of the series of anions in the salts analogous to **X** can be attributed to electron delocalization.

4.7 Draw one resonance structure with a significant contribution for the anion in each of the four salts. **4 pt**

Avogadro constant:	$N_A = 6.022 \cdot 10^{23}\ \text{mol}^{-1}$	Gas constant:	$R = 8.314\ \text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$
Ionic product of water at 298.15 K:	$K_w = 10^{-14}$	Zero of the Celsius scale:	$0^\circ\text{C} = 273.15\ \text{K}$
Faraday constant:	$F = 96485\ \text{C}\,\text{mol}^{-1}$	Planck constant:	$h = 6.626 \cdot 10^{-34}\ \text{J}\,\text{s}$
Speed of light:	$c = 2.998 \cdot 10^{8}\ \text{m}\,\text{s}^{-1}$	Standard pressure:	$p^\circ = 1 \cdot 10^5\ \text{Pa} = 1\ \text{bar}$
Ideal gas law:	$pV = nRT$	Beer-Lambert law:	$A = \log\left(\frac{I_0}{I}\right) = \varepsilon \cdot l \cdot c$
Enthalpy:	$H = U + pV$	Gibbs energy:	$G = H - TS$
$\Delta_r G^\circ = -RT\ln K = -nFE^\circ_{\text{cell}}$		Henderson-Hasselbalch equation:	$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$
Arrhenius equation:	$k = A\exp\left(-\frac{E_A}{RT}\right)$	Zeroth order integrated rate law:	$[\text{A}] = [\text{A}]_0 - kt$
Surface of a sphere:	$A = 4\pi R^2$	First order integrated rate law:	$\ln[\text{A}] = \ln[\text{A}]_0 - kt$
Volume of a sphere:	$V = \frac{4\pi}{3}R^3$	$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}$ for $\lvert r\rvert < 1$	

Periodic table



Official English text of the problem.

Answers

- **4.1** Cathode (1): $\boxed{\mathrm{K^+ + e^- \longrightarrow K}}$. Anode (2): $\boxed{\mathrm{4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^-}}$.
- **4.2** $\boxed{\mathrm{K_2CO_3 + 2\,C \longrightarrow 2\,K\,(g) + 3\,CO\,(g)}}$.
- **4.3** $\boxed{\mathrm{pH = -0.48}}$.
- **4.4** $\boxed{\mathrm{pH = 7.21}}$, including water autoionization at $298.15\ \mathrm{K}$.
- **4.5 X is potassium croconate dihydrate**, $\boxed{\mathrm{K_2C_5O_5 \cdot 2\,H_2O}}$, or $\mathrm{C_5H_4K_2O_7}$ as an elemental empirical formula. SMILES: `[K+].[K+].[O-]C1=C([O-])C(=O)C(=O)C1=O.O.O`.
- **4.6 Y is croconic acid**, $\boxed{\mathrm{C_5H_2O_5}}$, also named 4,5-dihydroxycyclopent-4-ene-1,2,3-trione. SMILES: `OC1=C(O)C(=O)C(=O)C1=O`.
- **4.7** One significant resonance contributor for each anion is specified below. Each has two adjacent, singly bonded negatively charged oxygen atoms, a double bond between their ring carbons, and carbonyl groups on all remaining ring carbons.

Anion	Formula	SMILES of one resonance contributor
Croconate	$\mathrm{C_5O_5^{2-}}$	`[O-]C1=C([O-])C(=O)C(=O)C1=O`
Squarate	$\mathrm{C_4O_4^{2-}}$	`[O-]C1=C([O-])C(=O)C1=O`
Deltate	$\mathrm{C_3O_3^{2-}}$	`[O-]C1=C([O-])C1=O`
Rhodizonate	$\mathrm{C_6O_6^{2-}}$	`[O-]C1=C([O-])C(=O)C(=O)C(=O)C1=O`

Solution

4.1

In molten potassium hydroxide, potassium cations gain electrons at the cathode:

$$\boxed{\mathrm{K^+ + e^- \longrightarrow K}}$$

Hydroxide ions lose electrons at the anode, forming oxygen and water:

$$\boxed{\mathrm{4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e^-}}$$

Both atoms and charge are balanced. Multiplying the cathode equation by four and adding gives the overall reaction:

$$\mathrm{4\,KOH \longrightarrow 4\,K + O_2 + 2\,H_2O}$$

The species are potassium hydroxide, `[K+].[OH-]`; potassium cation, `[K+]`; potassium, `[K]`; hydroxide ion, `[OH-]`; dioxygen, `O=O`; and water, `O`. The potassium atom SMILES does not describe bulk metallic bonding.

4.2

One formula unit of potassium carbonate supplies two potassium atoms and three oxygen atoms. Since carbon monoxide is the only oxygen-containing product, three molecules of carbon monoxide must form. They require two carbon atoms in addition to the carbonate carbon:

$$\boxed{\mathrm{K_2CO_3 + 2\,C \longrightarrow 2\,K\,(g) + 3\,CO\,(g)}}$$

Potassium carbonate has SMILES `[K+].[K+].[O-]C(=O)[O-]`; carbon monoxide has SMILES `[C-]#[O+]`. Elemental carbon is an extended solid and has no single molecular SMILES.

4.3

Write the diprotic acid as $\mathrm{H_2A}$, with equilibria

$$\mathrm{H_2A} \rightleftharpoons \mathrm{H^+} + \mathrm{HA^-}, \qquad \mathrm{HA^-} \rightleftharpoons \mathrm{H^+} + \mathrm{A^{2-}}.$$

Here $\mathrm{H^+}$, proton SMILES `[H+]`, is the conventional aqueous acid–base shorthand. The specific acid and anions are identified below.

Using the usual ideal-solution concentration treatment,

$$K_{a1} = 10^{-0.8} = 0.158489, \qquad K_{a2} = 10^{-2.2} = 0.00630957.$$

Let $h = [\mathrm{H^+}]$, with concentrations expressed in $\mathrm{mol\,dm^{-3}}$. The equilibrium ratios are

$$\frac{[\mathrm{HA^-}]}{[\mathrm{H_2A}]} = \frac{K_{a1}}{h}, \qquad \frac{[\mathrm{A^{2-}}]}{[\mathrm{H_2A}]} = \frac{K_{a1}K_{a2}}{h^2}.$$

Consequently, the fraction present as neutral acid is

$$\alpha_0 = \frac{[\mathrm{H_2A}]}{[\mathrm{H_2A}] + [\mathrm{HA^-}] + [\mathrm{A^{2-}}]} = \frac{h^2}{h^2 + K_{a1}h + K_{a1}K_{a2}}.$$

Setting $\alpha_0 = 0.95$ gives

$$h^2 - 19K_{a1}h - 19K_{a1}K_{a2} = 0.$$

The positive root is

$$h = \frac{19K_{a1} + \sqrt{(19K_{a1})^2 + 76K_{a1}K_{a2}}}{2} = 3.01759\ \mathrm{mol\,dm^{-3}}.$$

Thus

$$\boxed{\mathrm{pH} = -\log_{10}(3.01759) = -0.47966 \approx -0.48}.$$

The corresponding fractions are 0.950000, 0.049896, and 0.000104 for neutral acid, monoanion, and dianion. A negative pH is permissible.

4.4

The dipotassium salt supplies the dianion at analytical concentration

$$C = 0.010\ \mathrm{mol\,dm^{-3}}, \qquad [\mathrm{K^+}] = 2C.$$

Its main hydrolysis equilibrium is

$$\mathrm{A^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{HA^-} + \mathrm{OH^-},$$

with

$$K_b = \frac{K_w}{K_{a2}} = \frac{10^{-14}}{10^{-2.2}} = 1.58489 \times 10^{-12}.$$

The estimate $\sqrt{K_bC} = 1.26 \times 10^{-7}\ \mathrm{mol\,dm^{-3}}$ is comparable to the hydroxide concentration in pure water. **Water autoionization must therefore be retained.**

The material and charge balances are

$$C = [\mathrm{H_2A}] + [\mathrm{HA^-}] + [\mathrm{A^{2-}}]$$

and

$$2C + h = [\mathrm{HA^-}] + 2[\mathrm{A^{2-}}] + [\mathrm{OH^-}].$$

Eliminating C,

$$[\mathrm{OH^-}] = h + [\mathrm{HA^-}] + 2[\mathrm{H_2A}].$$

At approximately neutral pH, both acid dissociation constants are much greater than h. Thus nearly all the acid-derived material remains as dianion:

$$[\mathrm{A^{2-}}] \simeq C, \qquad [\mathrm{HA^-}] \simeq \frac{Ch}{K_{a2}}, \qquad [\mathrm{H_2A}] \ll [\mathrm{HA^-}].$$

Using $[\mathrm{OH^-}] = K_w/h$,

$$\frac{K_w}{h} \simeq h + \frac{Ch}{K_{a2}},$$

so

$$h \simeq \sqrt{\frac{K_w}{1 + C/K_{a2}}} = \sqrt{\frac{10^{-14}}{1 + 0.010/0.00630957}} = 6.22 \times 10^{-8}\ \mathrm{mol\,dm^{-3}}.$$

Therefore,

$$\boxed{\mathrm{pH} = 7.2062 \approx 7.21}.$$

As a check,

$$[\mathrm{OH^-}] \approx 1.61 \times 10^{-7}\ \mathrm{mol\,dm^{-3}}, \qquad [\mathrm{HA^-}] \approx 9.86 \times 10^{-8}\ \mathrm{mol\,dm^{-3}}.$$

Only about 9.86×10^{-6} of the analytical acid concentration is monoanion, validating the approximation $[\mathrm{A^{2-}}] \simeq C$. Solving the full equilibria and charge balance gives the same pH to the precision reported.

4.5

Reaction with two equivalents of methyl iodide introduces two methyl groups into the dianion. Using the supplied atomic masses,

$$M(\mathrm{CH_3}) = 12.01 + 3(1.008) = 15.034\ \mathrm{g\,mol^{-1}}.$$

The mass of the anionic framework in **X** is therefore

$$170.12 - 2(15.034) = 140.052\ \mathrm{g\,mol^{-1}}.$$

The derivative masses differ by multiples of

$$28.01\ \mathrm{g\,mol^{-1}} = 12.01 + 16.00,$$

the mass of one carbon–oxygen unit. Removing the two methyl groups from each derivative gives:

Derivative molar mass / $\mathrm{g\,mol^{-1}}$	Framework molar mass / $\mathrm{g\,mol^{-1}}$	Number of carbon–oxygen units	Anion
170.12	140.05	5	Croconate, $\mathrm{C_5O_5^{2-}}$
142.11	112.04	4	Squarate, $\mathrm{C_4O_4^{2-}}$
114.10	84.03	3	Deltate, $\mathrm{C_3O_3^{2-}}$
198.13	168.06	6	Rhodizonate, $\mathrm{C_6O_6^{2-}}$

Together with the stated planar cyclic symmetry, these masses identify the cyclic oxocarbon dianions: rings of carbon atoms bearing one exocyclic oxygen per carbon.

For **X**, the framework is $\mathrm{C_5O_5^{2-}}$. Two potassium cations balance its charge, and the stated hydration adds two water molecules:

$$\boxed{\mathrm{X = K_2C_5O_5 \cdot 2\,H_2O}}.$$

Its elemental empirical formula is equivalently

$$\boxed{\mathrm{C_5H_4K_2O_7}}.$$

The compound is **potassium croconate dihydrate**, SMILES `[K+].[K+].[O-]C1=C([O-])C(=O)C(=O)C1=O.O.O`. This notation specifies the components and one anion resonance contributor; it does not specify the crystal lattice or water coordination.

The methylation is

$$\mathrm{K_2C_5O_5 + 2\,CH_3I \longrightarrow C_5O_3(OCH_3)_2 + 2\,KI}.$$

The organic product is **dimethyl croconate**, SMILES `COC1=C(OC)C(=O)C(=O)C1=O`. Methyl iodide is `CI`, and potassium iodide is `[K+].[I-]`. The calculated product mass is

$$M(\mathrm{C_7H_6O_5}) = 7(12.01) + 6(1.008) + 5(16.00) = 170.118\ \mathrm{g\,mol^{-1}},$$

which rounds to the given $170.12\ \mathrm{g\,mol^{-1}}$.

4.6

Protonating the two negatively charged oxygen atoms of a croconate resonance contributor gives **croconic acid**, $\mathrm{C_5H_2O_5}$:

$$\mathrm{C_5O_5^{2-} + 2\,H^+ \longrightarrow C_5H_2O_5}.$$

Its name is **4,5-dihydroxycyclopent-4-ene-1,2,3-trione**, and its SMILES is:

`OC1=C(O)C(=O)C(=O)C1=O`

To draw it precisely:

1. Draw a five-carbon ring numbered consecutively 1–5.
2. Put an exocyclic carbonyl oxygen on each of carbons 1, 2, and 3.
3. Put a double bond between carbons 4 and 5.
4. Attach one hydroxyl group to carbon 4 and one to carbon 5.
5. All remaining ring bonds are single; no hydrogen is bonded directly to a ring carbon.

The acid–base species used in 4.3–4.4 are therefore croconic acid, hydrogen croconate, and croconate. **Hydrogen croconate**, $\mathrm{C_5HO_5^-}$, has the representative SMILES `[O-]C1=C(O)C(=O)C(=O)C1=O`.

The low $\mathrm{p}K_a$ values are consistent with stabilization of the conjugate bases by electron delocalization through the conjugated carbon–oxygen framework.

4.7

For every anion, a significant contributor can be drawn by the same construction:

- Draw a ring of n carbon atoms.
- Choose two adjacent ring carbons and join them by a double bond.
- Attach a singly bonded $\mathrm{O^-}$ to each of those two carbons.
- Attach an exocyclic carbonyl oxygen to every remaining ring carbon.
- Make every other ring bond single.

This gives the following precise drawings:

Anion	Carbon ring	Groups on the two double-bonded ring carbons	Groups on the remaining ring carbons
Croconate	Five-membered	Two singly bonded $\mathrm{O^-}$ atoms	Three carbonyls
Squarate	Four-membered	Two singly bonded $\mathrm{O^-}$ atoms	Two carbonyls
Deltate	Three-membered	Two singly bonded $\mathrm{O^-}$ atoms	One carbonyl

Anion	Carbon ring	Groups on the two double-bonded ring carbons	Groups on the remaining ring carbons
Rhodizonate	Six-membered	Two singly bonded $\mathrm{O^-}$ atoms	Four carbonyls

The corresponding names, formulas, and explicit SMILES are given in **Answers, 4.7**. In each contributor, every carbon and oxygen has an octet, the net charge is -2, and both formal negative charges lie on oxygen.

Electron-pair shifts generate other resonance contributors without moving atoms. For example, an anionic oxygen lone pair can form a carbonyl bond while the neighboring ring double bond shifts and another carbonyl π-electron pair moves onto oxygen. This relocates the formal negative charges around the conjugated framework.

The actual ions are resonance hybrids. The localized SMILES do not show their planar geometry, delocalized charge, or bond equalization; in particular, a single localized contributor does not display the full symmetry of croconate.

The solution was checked against the official solution.

Problem 5: Unknown

Metal containing salt **A** can be prepared in a simple exchange reaction when the cold, saturated aqueous solutions of the two distinctly colored compounds, **B** and **C** are mixed in stoichiometric ratio. 10.00 g **B** in solution mixed with the solution of 12.86 g **C**, and immediately cooled to $2\ ^\circ\mathrm{C}$ will give 4.90 g solid **A**. The yield of **A** is 32.6 %.

To determine the composition of **A**, first iodometry is performed. A known mass of **A** is added to a titration flask, acidified with sulfuric acid, then KI is added in excess and there is a precipitate formation. After a few minutes, sodium citrate solution is added until the solution is free of precipitate. The citrate ions form a strong complex with a metal ion present in the mixture, reversing completely the reaction leading to the precipitate. The resulting mixture is titrated with sodium thiosulfate solution (Titration I via reaction 1). To the blue titrated solution another portion of sulfuric acid (significantly more than the initial amount) is added to protonate the citrate. The previous solid precipitate is formed once again [reaction 2]. The mixture is titrated with the same thiosulfate solution (titration II via reaction 1).

The average volumes for 100.0 mg **A** with $5.000 \cdot 10^{-2}\ \mathrm{mol\,dm^{-3}}$ thiosulfate are $54.12\ \mathrm{cm^3}$ in Titration I and $5.41\ \mathrm{cm^3}$ in Titration II.

When the aqueous solution of **A** is heated, the blue precipitate **D** can be observed [reaction 3]. Compound **E** can be crystallized from the liquid above **D**. The low temperature during the synthesis of **A** is important to avoid contamination by **E**.

5.1 Write balanced equations for reactions [1] and [2]. 4.0 pt

The thermal decomposition of **A** was studied in detail. When pure **A** is slowly heated, already at around $75\ ^\circ\mathrm{C}$ it explodes. When the compound is dispersed in aluminium oxide and the mixture is heated, then the matrix absorbs the excess heat, and the explosion can be avoided. Two decomposition steps can be observed. In the first step (at $65\ ^\circ\mathrm{C}$) in addition to the 14.1 % mass decrease, a two-component solid residue forms [reaction 4]. The components of this residue can be easily separated, as **F** is well soluble in water, while **G** does not dissolve at all. The **F**:**G** mass ratio is 1.00 : 2.97. On further heating, **F** decomposes without a solid residue [reaction 5]. That means pure **G** is the final solid decomposition product of **A**. **G** contains two other elements in addition to 27.0 wt% oxygen. One of the two components of the gas mixture forming in the first decomposition step can be easily quantitated if it is absorbed in acid solution.

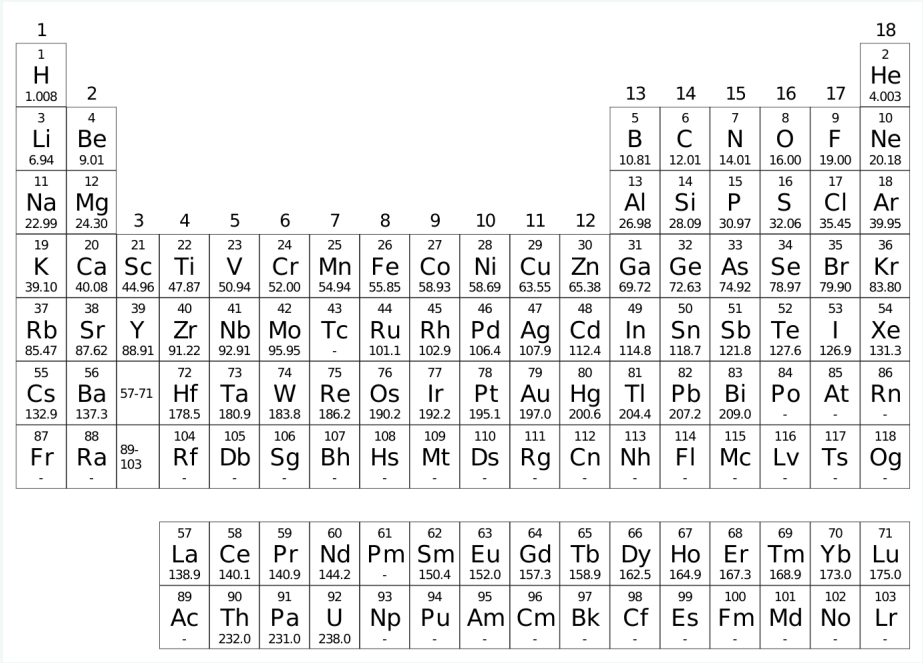
Some hints

- Compound **A** decomposes without releasing oxygen.
- Compound **A** contains two different metals.
- Compounds **A** and **B** both contain a complex ion.
- **C** is a well-known compound for any chemistry student.
- Compound **F** does not contain any metal.

5.2 Give chemical formulae of A—G. You don't have to show your calculations, but if your compounds are incorrect you may gain partial marks from correct calculations. **28.0 pt**

5.3 Write balanced equations for reactions [3]—[5]. 12.0 pt

Periodic table



Official English text of the problem.

Answers

- **5.1 — Reactions [1] and [2]**

$$\boxed{\mathrm{I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}}} \tag{1}$$

$$\boxed{\mathrm{2\,Cu^{2+} + 4\,I^- \longrightarrow 2\,CuI(s) + I_2}} \tag{2}$$

- **5.2 — Formulae of A–G**

Compound	Formula	Name	SMILES or formal formula-unit representation
A	$\mathrm{[Cu(NH_3)_4](MnO_4)_2}$	Tetraamminecopper(II) permanganate	`[Cu+2](<-[NH3])(<-[NH3])(<-[NH3])<-[NH3].[O-][Mn](=O)(=O)=O.[O-][Mn](=O)(=O)=O`
B	$\mathrm{[Cu(NH_3)_4]SO_4 \cdot H_2O}$	Tetraamminecopper(II) sulfate monohydrate	`[Cu+2](<-[NH3])(<-[NH3])(<-[NH3])<-[NH3].[O-]S(=O)(=O)[O-].O`
C	$\mathrm{KMnO_4}$	Potassium permanganate	`[K+].[O-][Mn](=O)(=O)=O`
D	$\mathrm{Cu(OH)_2}$	Copper(II) hydroxide	`[Cu+2].[OH-].[OH-]`
E	$\mathrm{NH_4MnO_4}$	Ammonium permanganate	`[NH4+].[O-][Mn](=O)(=O)=O`
F	$\mathrm{NH_4NO_3}$	Ammonium nitrate	`[NH4+].[O-][N+](=O)[O-]`
G	$\mathrm{CuMn_2O_4}$	Copper manganese oxide, or copper manganite	Formal ionic inventory: `[Cu+2].[Mn+3].[Mn+3].[O-2].[O-2].[O-2].[O-2]`

Dative-bond SMILES use <- for donation from ammonia to copper. The four nitrogen donors form an approximately square-planar $\mathrm{CuN_4}$ unit; the strings do not specify axial crystal contacts. Dot-separated representations give ionic composition. **D** and **G** are extended solids, so their entries specify formula-unit inventories rather than discrete molecular structures.

- **5.3 — Reactions [3]–[5]**

$$\boxed{\mathrm{[Cu(NH_3)_4](MnO_4)_2 + 2\,H_2O \xrightarrow{\Delta} Cu(OH)_2\,(s) + 2\,NH_4MnO_4 + 2\,NH_3}} \tag{3}$$

$$\boxed{\mathrm{[Cu(NH_3)_4](MnO_4)_2 \xrightarrow{\Delta} CuMn_2O_4\,(s) + NH_4NO_3\,(s) + 2\,NH_3\,(g) + H_2O\,(g)}} \tag{4}$$

$$\boxed{\mathrm{NH_4NO_3 \xrightarrow{\Delta} N_2O\,(g) + 2\,H_2O\,(g)}} \tag{5}$$

Solution

5.1 — Identifying the iodometric reactions

The blue solution and the formation of an insoluble iodide identify copper(II). Iodide reduces copper(II) to copper(I), which precipitates as copper(I) iodide:

$$\mathrm{2\,Cu^{2+} + 4\,I^- \longrightarrow 2\,CuI(s) + I_2}.$$

The iodine is titrated with thiosulfate, producing tetrathionate:

$$\mathrm{I_2} + 2\,{\mathrm{S_2O_3}}^{2-} \longrightarrow 2\,\mathrm{I^-} + {\mathrm{S_4O_6}}^{2-}.$$

The molecular and ionic species in these equations are:

Species	Name	SMILES
$\mathrm{Cu^{2+}}$	Copper(II) ion	`[Cu+2]`
CuI	Copper(I) iodide	`[Cu+].[I-]`
$\mathrm{I^-}$	Iodide ion	`[I-]`
$\mathrm{I_2}$	Iodine	`II`
${\mathrm{S_2O_3}}^{2-}$	Thiosulfate ion	`[O-]S(=O)(=O)[S-]`
${\mathrm{S_4O_6}}^{2-}$	Tetrathionate ion	`[O-]S(=O)(=O)SSS(=O)(=O)[O-]`

Citrate, ${\mathrm{C_6H_5O_7}}^{3-}$, SMILES `[O-]C(=O)CC(O)(CC(=O)[O-])C(=O)[O-]`, strongly complexes copper(II). Removing free copper(II) shifts reaction [2] backwards: copper(I) iodide dissolves, and the iodine originally generated by copper(II) is consumed.

Consequently, **Titration I measures the other oxidizing component of A**. Subsequent acidification protonates citrate, releases copper(II), and permits reaction [2] to occur again. **Titration II therefore measures copper alone.**

Combining reactions [1] and [2] shows that one mole of copper(II) corresponds to one mole of thiosulfate in Titration II.

5.2 — Identifying A–G

The calculations below use the supplied atomic masses; intermediate results retain guard digits.

Copper content and the composition of G.

For the $100.0\ \mathrm{mg}$ sample,

$$\begin{aligned} n_{\mathrm{I}}({\mathrm{S_2O_3}}^{2-}) &= (5.000 \times 10^{-2})(54.12 \times 10^{-3}) \\ &= 2.706 \times 10^{-3}\ \mathrm{mol}, \end{aligned}$$

$$\begin{aligned} n_{\mathrm{II}}({\mathrm{S_2O_3}}^{2-}) &= (5.000 \times 10^{-2})(5.41 \times 10^{-3}) \\ &= 2.705 \times 10^{-4}\ \mathrm{mol}. \end{aligned}$$

Thus,

$$n(\mathrm{Cu}) = 2.705 \times 10^{-4}\ \mathrm{mol}, \qquad m(\mathrm{Cu}) = 17.19\ \mathrm{mg}.$$

The first decomposition step leaves 85.9% of the original mass. Using the stated **F:G** mass ratio, the amount of **G** obtained from $100.0\ \mathrm{mg}$ of **A** is

$$m(\mathrm{G}) = (100.0\ \mathrm{mg})(0.859)\frac{2.97}{1.00 + 2.97} = 64.26\ \mathrm{mg}.$$

Its oxygen content is

$$m(\mathrm{O}) = (0.270)(64.26) = 17.35\ \mathrm{mg}.$$

Therefore,

$$\frac{n(\mathrm{O})}{n(\mathrm{Cu})} = \frac{0.01735/16.00}{2.705 \times 10^{-4}} = 4.009 \approx 4.$$

The remaining mass belongs to the second metal:

$$m(\text{second metal}) = 64.26 - 17.35 - 17.19 = 29.72\ \mathrm{mg}.$$

Per mole of copper, this is

$$\frac{0.02972}{2.705 \times 10^{-4}} = 109.88\ \mathrm{g\,mol^{-1}} = 2(54.94)\ \mathrm{g\,mol^{-1}}.$$

This identifies **two manganese atoms per copper atom**, giving

$$\boxed{\mathrm{G = CuMn_2O_4}}.$$

The calculated oxygen percentage confirms the assignment:

$$M(\mathrm{G}) = 63.55 + 2(54.94) + 4(16.00) = 237.43\ \mathrm{g\,mol^{-1}},$$

$$w_{\mathrm{O}}(\mathrm{G}) = \frac{64.00}{237.43} \times 100\% = 26.955\% \approx 27.0\%.$$

The oxidizing anion and the complex in A.

The titration-volume ratio is

$$\frac{n_{\mathrm{I}}}{n_{\mathrm{II}}} = \frac{54.12}{5.41} = 10.00.$$

Thus, the non-copper oxidant accepts ten electrons per copper atom. Since there are two manganese atoms per copper atom, each manganese accepts five electrons. This identifies the acidic reduction of permanganate to manganese(II):

$$2\,{\mathrm{MnO_4}}^{-} + 16\,\mathrm{H^+} + 10\,\mathrm{I^-} \longrightarrow 2\,\mathrm{Mn^{2+}} + 5\,\mathrm{I_2} + 8\,\mathrm{H_2O}.$$

Here the permanganate ion is ${\mathrm{MnO_4}}^{-}$, SMILES `[O-][Mn](=O)(=O)=O`; manganese(II) is `[Mn+2]`, and a proton is `[H+]`. Permanganate has tetrahedral coordination around manganese; its SMILES gives one localized resonance representation.

One permanganate ion generates iodine requiring five thiosulfate ions. Independently,

$$n(\mathrm{MnO_4^-}) = \frac{2.706\times10^{-3}}{5} = 5.412\times10^{-4}\ \mathrm{mol},$$
$$\frac{n(\mathrm{MnO_4^-})}{n(\mathrm{Cu})} = \frac{5.412\times10^{-4}}{2.705\times10^{-4}} = 2.001 \approx 2.$$

The mass of **A** per mole of copper is

$$\frac{0.1000\ \mathrm{g}}{2.705\times10^{-4}\ \mathrm{mol}} = 369.7\ \mathrm{g\,mol^{-1}}.$$

Subtracting one copper and two permanganates leaves approximately

$$369.7 - 63.55 - 2(54.94 + 64.00) = 68.3\ \mathrm{g\,mol^{-1}}.$$

The acid-absorbable gas suggests ammonia, $\mathrm{NH_3}$, SMILES `N`. Four ammonia ligands contribute

$$4M(\mathrm{NH_3}) = 4[14.01 + 3(1.008)] = 68.136\ \mathrm{g\,mol^{-1}}.$$

Hence the complex ion is tetraamminecopper(II),

$$[\mathrm{Cu(NH_3)_4}]^{2+},$$

SMILES `[Cu+2](<-[NH3])(<-[NH3])(<-[NH3])<-[NH3]`, and

$$\boxed{\mathrm{A} = [\mathrm{Cu(NH_3)_4}](\mathrm{MnO_4})_2}.$$

Its calculated molar mass is

$$M(\mathrm{A}) = 369.566\ \mathrm{g\,mol^{-1}}.$$

This formula predicts

$$V_{\mathrm{I}} = \frac{10(0.1000/369.566)}{0.05000} = 0.0541175\ \mathrm{dm^3} = 54.12\ \mathrm{cm^3},$$
$$V_{\mathrm{II}} = \frac{0.1000/369.566}{0.05000} = 0.00541175\ \mathrm{dm^3} = 5.41\ \mathrm{cm^3},$$

matching both titrations.

Identifying B and C from the preparation.

The theoretical mass of **A** is

$$m_{\mathrm{theor}}(\mathrm{A}) = \frac{4.90}{0.326} = 15.0307\ \mathrm{g},$$

corresponding to

$$n_{\mathrm{theor}}(\mathrm{A}) = \frac{15.0307}{369.566} = 0.0406712\ \mathrm{mol}.$$

In the exchange reaction, **B** supplies one tetraamminecopper(II) ion per formula unit of **A**, while two formula units of the monovalent permanganate salt **C** are required. The inferred molar masses are therefore

$$M(\mathrm{B}) \approx \frac{10.00}{0.0406712} = 245.9\ \mathrm{g\,mol^{-1}},$$
$$M(\mathrm{C}) \approx \frac{12.86}{2(0.0406712)} = 158.1\ \mathrm{g\,mol^{-1}}.$$

The familiar purple compound **C** is potassium permanganate:

$$M(\mathrm{KMnO_4}) = 39.10 + 54.94 + 64.00 = 158.04\ \mathrm{g\,mol^{-1}}.$$

The deep-blue copper ammine salt matching **B** is tetraamminecopper(II) sulfate monohydrate:

$$M([\mathrm{Cu(NH_3)_4}]\mathrm{SO_4}\cdot\mathrm{H_2O}) = 63.55 + 4(17.034) + 96.06 + 18.016$$
$$= 245.762\ \mathrm{g\,mol^{-1}}.$$

Thus,

$$\boxed{\mathrm{B} = [\mathrm{Cu(NH_3)_4}]\mathrm{SO_4}\cdot\mathrm{H_2O}}, \qquad \boxed{\mathrm{C} = \mathrm{KMnO_4}}.$$

The preparation is

$$[\mathrm{Cu(NH_3)_4}]\mathrm{SO_4}\cdot\mathrm{H_2O} + 2\,\mathrm{KMnO_4} \longrightarrow [\mathrm{Cu(NH_3)_4}](\mathrm{MnO_4})_2\,(\mathrm{s}) + \mathrm{K_2SO_4} + \mathrm{H_2O}.$$

The other salt is potassium sulfate, $\mathrm{K_2SO_4}$, SMILES `[K+].[K+].[O-]S(=O)(=O)[O-]`. Water has SMILES `O`.

Checking the given quantities:

$$m(\mathrm{C}) = \frac{10.00}{245.762}(2)(158.04) = 12.861\ \mathrm{g},$$
$$m_{\mathrm{isolated}}(\mathrm{A}) = \frac{10.00}{245.762}(369.566)(0.326) = 4.902\ \mathrm{g},$$

which round to 12.86 g and 4.90 g.

Identifying D and E.

Heating the aqueous ammine complex promotes ammonia loss. The blue copper-containing precipitate is copper(II) hydroxide:

$$\boxed{\mathrm{D} = \mathrm{Cu(OH)_2}}.$$

Formation of one formula unit of hydroxide uses two water molecules. Two ammonia ligands become ammonium ions, and the other two are released as ammonia. The two permanganate ions consequently remain with ammonium:

$$\boxed{\mathrm{E} = \mathrm{NH_4MnO_4}}.$$

The ammonium ion, $\mathrm{NH_4}^+$, has SMILES `[NH4+]`. This explains why warming the synthesis mixture can introduce **E** as a contaminant.

Identifying F.

One formula unit of **A** gives one formula unit of **G**. From the residue mass ratio, the mass of **F** accompanying one mole of **G** is

$$\frac{237.43}{2.97} = 79.94\ \mathrm{g}.$$

This matches one mole of ammonium nitrate:

$$M(\mathrm{NH_4NO_3}) = 2(14.01) + 4(1.008) + 3(16.00) = 80.052\ \mathrm{g\,mol^{-1}}.$$

Ammonium nitrate is water-soluble, contains no metal, and decomposes into gaseous products. Therefore,

$$\boxed{\mathrm{F} = \mathrm{NH_4NO_3}}.$$

Its nitrate ion, $\mathrm{NO_3}^-$, has SMILES `[O-][N+](=O)[O-]`; the ion is trigonal planar with delocalized bonding.

5.3 — Aqueous and thermal decomposition equations

For aqueous decomposition, the assignments of **D** and **E** give

$$\boxed{[\mathrm{Cu(NH_3)_4}](\mathrm{MnO_4})_2 + 2\,\mathrm{H_2O} \xrightarrow{\Delta} \mathrm{Cu(OH)_2\,(s)} + 2\,\mathrm{NH_4MnO_4} + 2\,\mathrm{NH_3}}. \tag{3}$$

For the first thermal decomposition, subtracting $\mathrm{CuMn_2O_4}$ and $\mathrm{NH_4NO_3}$ from the composition of **A** leaves exactly two ammonia molecules and one water molecule:

$$\boxed{[\mathrm{Cu(NH_3)_4}](\mathrm{MnO_4})_2 \xrightarrow{\Delta} \mathrm{CuMn_2O_4\,(s)} + \mathrm{NH_4NO_3\,(s)} + 2\,\mathrm{NH_3\,(g)} + \mathrm{H_2O\,(g)}}. \tag{4}$$

The predicted mass decrease is

$$\frac{2M(\mathrm{NH_3}) + M(\mathrm{H_2O})}{M(\mathrm{A})} \times 100\% = \frac{2(17.034) + 18.016}{369.566} \times 100\% = 14.093\% \approx 14.1\%.$$

The predicted solid mass ratio is

$$m(\mathrm{F}) : m(\mathrm{G}) = 80.052 : 237.43 = 1.00 : 2.966 \approx 1.00 : 2.97.$$

The gas readily quantified by absorption in acid is ammonia:

$$\mathrm{NH_3} + \mathrm{H^+} \longrightarrow \mathrm{NH_4}^+.$$

Reaction [4] is also consistent with internal electron transfer: two manganese atoms are reduced from $+7$ to the formal $+3$ state, accepting eight electrons in total, while one ammine nitrogen is oxidized from -3 to $+5$ in nitrate, releasing eight electrons.

Finally, ammonium nitrate decomposes without a solid residue or oxygen evolution:

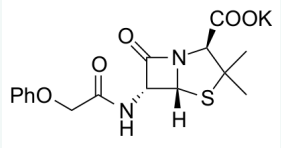
$$\boxed{\mathrm{NH_4NO_3} \xrightarrow{\Delta} \mathrm{N_2O\,(g)} + 2\,\mathrm{H_2O\,(g)}}. \tag{5}$$

The nitrogen-containing gas is **nitrous oxide**, $\mathrm{N_2O}$, SMILES `N#[N+][O-]`. It has a linear N–N–O arrangement; the SMILES represents one resonance form.

The solution was checked against the official solution.

Problem 6: Penicillin

Penicillins are a group of antibiotics that have played a crucial role in medicine since their discovery.



Penicillin VK

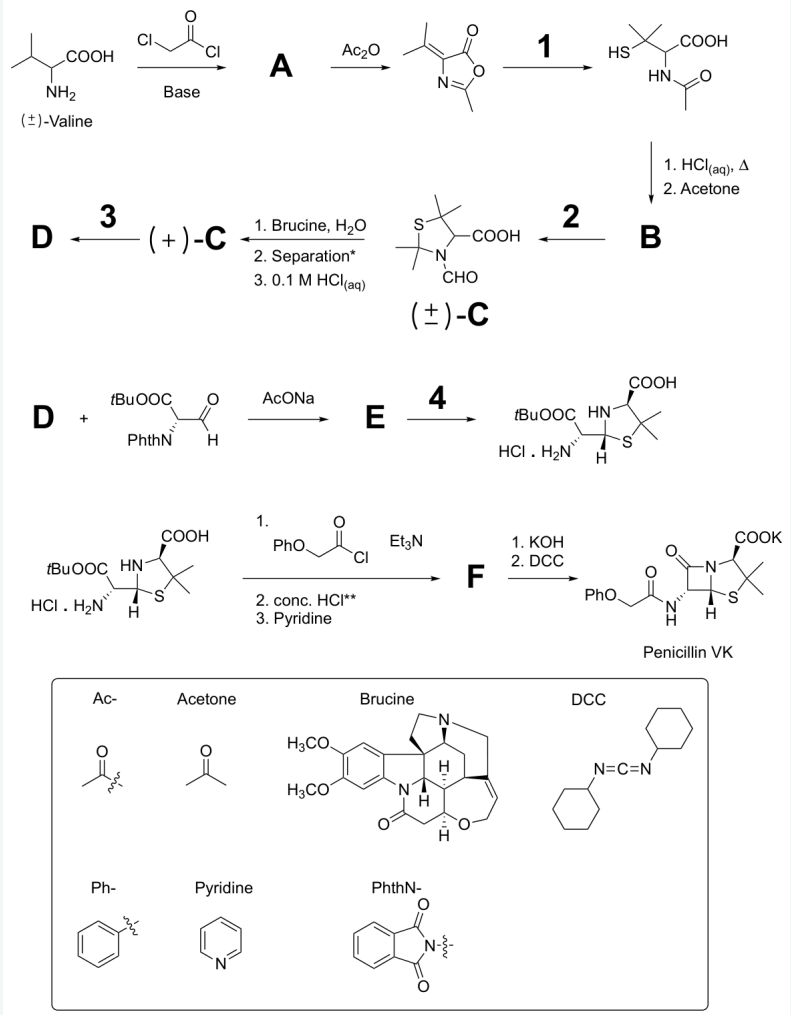
6.1. Mark the stereogenic carbon centers on the structure of Penicillin VK on the answer sheet. **Write** the corresponding R/S stereodescriptors next to the centers on the answer sheet. **6 pt**

6.2. Give the total number of possible stereoisomers of Penicillin VK. **2 pt**

One of the many synthetic methods to obtain Penicillin VK starts from the amino acid valine, as shown in the scheme on the next page of this problem.

Hints:

- Among other signals, the ^{1}HNMR spectrum of compound **A** contains two signals that each integrate to 3H. Both of these signals are doublets.
- Compounds **A** and **D** are open-chain compounds, while **B** and **E** each have a five membered ring (in addition to any rings in the PhthN-group).
- Brucine is used for chiral resolution.



*Please note that in the formation of **(+)-C**, the word "Separation" means **separation**.

Conc. HCl means **concentrated HCl.

6.3. Choose the suitable reagent for the numbered steps $(1–4)$ on the answer sheet. **8 pt**

a) $2\,\mathrm{M\ HCl_{(aq)}}$

b) $\mathrm{SO_3}$, $\mathrm{H_2SO_4}$

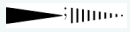
c) $\mathrm{NaOH_{(aq)}}$

d) $\mathrm{HCO_2H}$, $\mathrm{Ac_2O}$

e) i) $\mathrm{N_2H_4}$ ii) $\mathrm{HCl_{(aq)}}$, AcOH

f) i) $\mathrm{H_2S}$, Na, $\mathrm{CH_3OH}$ ii) $\mathrm{H_2O}$

6.4. Draw the structures of **A, B, (+)-C, D, E** and **F** on the answer sheet. **Show** the stereostructure using wedge–dash notation (



) when relevant. **18 pt**

6.5. Select the role of acetone in the step leading to **B** on the answer sheet. **2 pt**

a) solvent

b) catalyst

c) electrophile

d) nucleophile

6.6. Select the role of DCC in the step leading from **F** to Penicillin VK on the answer sheet. **2 pt**

a) oxidizing reagent

b) catalyst

c) coupling reagent

d) radical initiator

Official English text of the problem.

Answers

- **6.1.** There are **three stereogenic carbon centers**, with configuration $(2S, 5R, 6R)$ in standard penam numbering:
- Carboxylate-bearing carbon: S.
- Fused-ring carbon bearing the explicitly drawn hydrogen: R.
- β-Lactam carbon bearing the phenoxyacetamido substituent: R.
- **6.2.** 8 stereoisomers.
- **6.3. 1 → f; 2 → d; 3 → a; 4 → e.**
- **6.4.** The structures are given below. **A** and **B** are racemates; their SMILES specify connectivity without selecting one enantiomer.

Compound	Name	SMILES
A	$(\pm)$-N-(2-Chloroacetyl)valine	`CC(C)C(NC(=O)CCl)C(=O)O`
B	$(\pm)$-2,2,5,5-Tetramethyl-1,3-thiazolidine-4-carboxylic acid	`CC1(C)NC(C(=O)O)C(C)(C)S1`
(+)-C	$(4S)$-3-Formyl-2,2,5,5-tetramethyl-1,3-thiazolidine-4-carboxylic acid	`CC1(C)N(C=O)[C@@H](C(=O)O)C(C)(C)S1`
D	$(2S)$-2-Amino-3-methyl-3-sulfanylbutanoic acid, **D-penicillamine**	`CC(C)(S)[C@@H](N)C(=O)O`
E	$(2R, 4S)$-2-[$(1R)$-2-tert-butoxy-1-(1,3-dioxoisoindolin-2-yl)-2-oxoethyl]-5,5-dimethyl-1,3-thiazolidine-4-carboxylic acid	`CC(C)(C)OC(=O)[C@@H](N1C(=O)c2ccccc2C1=O)[C@H]1SC(C)(C)[C@H](C(=O)O)N1`
F	**Penicilloic acid V**: $(2R, 4S)$-2-[(R)-carboxy(2-phenoxyacetamido)methyl]-5,5-dimethyl-1,3-thiazolidine-4-carboxylic acid	`O=C(O)[C@@H](NC(=O)COc1ccccc1)[C@H]1SC(C)(C)[C@H](C(=O)O)N1`

D is shown above as its neutral parent. In the acidic mixture from step 3, it is **D-penicillamine hydrochloride**, `CC(C)(S)[C@@H]([NH3+])C(=O)O.[Cl-]`.

- **6.5. c) electrophile.**
- **6.6. c) coupling reagent.**

Solution

6.1. Stereogenic centers and absolute configurations

Penicillin VK is potassium $(2S, 5R, 6R)$-6-(2-phenoxyacetamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate:

`CC1(C)S[C@@H]2[C@H](NC(=O)COc3ccccc3)C(=O)N2[C@H]1C(=O)[O-].[K+]`

The three stereogenic carbons and their CIP priorities are:

Center	Position in the supplied drawing	Priorities, highest to lowest	Configuration
C_2	Upper-right carbon bearing the carboxylate	Ring nitrogen; gem-dimethyl carbon; carboxylate carbon; hydrogen	S
C_5	Fused-ring carbon bearing the solid-wedge hydrogen	Sulfur; ring nitrogen; C_6; hydrogen	R
C_6	β-Lactam carbon bearing the dashed-bond amide substituent	Side-chain nitrogen; C_5; β-lactam carbonyl carbon; hydrogen	R

Two carbon-versus-carbon comparisons deserve attention:

- At C_2, the gem-dimethyl carbon has the next-layer atoms $(\mathrm{S}, \mathrm{C}, \mathrm{C})$, whereas the carboxylate carbon has oxygen atoms. Sulfur gives the former higher priority.
- At C_6, the C_5 branch presents $(\mathrm{S}, \mathrm{N}, \mathrm{H})$, whereas the carbonyl branch presents $(\mathrm{O}, \mathrm{O}, \mathrm{N})$. Again, the sulfur-containing branch has higher priority.

Applying these priorities to the shown wedges and dashes gives $(2S, 5R, 6R)$. The carbon bearing two methyl groups is not stereogenic because those two substituents are identical.

6.2. Number of stereoisomers

There are three stereogenic carbon centers and no internal symmetry that produces a meso form. Therefore,

$$N_{\text{stereoisomers}} = 2^3 = \boxed{8}.$$

These comprise four enantiomeric pairs.

6.3. Identification of reagents

Step	Choice and reagents, with SMILES	Reason
1	**f**: hydrogen sulfide `S`, sodium `[Na]`, methanol `CO`; then water `O`	Introduces the thiol group at the carbon bearing two methyl groups; subsequent hydrolysis opens the oxazolone.
2	**d**: formic acid `O=CO`, acetic anhydride `CC(=O)OC(C)=O`	Formylates the thiazolidine nitrogen, producing the shown N-formyl compound **C**.
3	**a**: $2\,\mathrm{M}$ aqueous hydrochloric acid; hydrogen chloride `Cl`	Hydrolyzes the N-formyl group and the acetone-derived cyclic N, S-acetal, releasing open-chain penicillamine.
4	**e**: hydrazine `NN`; then hydrochloric acid `Cl` and acetic acid `CC(=O)O`	Removes the phthaloyl protecting group by hydrazinolysis and gives the amino ester hydrochloride.

The molecular SMILES `Cl` denotes hydrogen chloride. Its aqueous ionized representation is hydronium chloride, `[OH3+].[Cl-]`.

6.4. Structures and reaction sequence

The equations below are balanced net equations. Neutral parent structures are used unless a hydrochloride is explicitly indicated.

Formation of A and the oxazolone. Racemic valine, 2-amino-3-methylbutanoic acid, `CC(C)C(N)C(=O)O`, undergoes nitrogen acylation with chloroacetyl chloride, `O=C(Cl)CCl`:

$$(\mathrm{CH_3})_2\mathrm{CHCH(NH_2)COOH} + \mathrm{ClCH_2COCl} \longrightarrow \mathrm{A} + \mathrm{HCl}.$$

The supplied base traps the hydrogen chloride. Thus **A** is N-(2-chloroacetyl)valine.

The isopropyl group remains intact. Each methyl group couples to the adjacent methine proton, giving a doublet integrating to three hydrogens. The two methyl groups can have different chemical shifts because the molecule contains the neighboring stereogenic α-carbon. This agrees with the NMR hint.

Let **U** denote the drawn oxazolone, 2-methyl-4-(propan-2-ylidene)-1,3-oxazol-5(4H)-one:

`CC1=NC(=C(C)C)C(=O)O1`

Its formation involves cyclodehydration and loss of hydrogen chloride. Including acetic anhydride as the dehydrating reagent gives the net balance

$$\mathrm{A} + (\mathrm{CH_3CO})_2\mathrm{O} \longrightarrow \mathrm{U} + 2\,\mathrm{CH_3COOH} + \mathrm{HCl}.$$

Sulfur introduction and formation of B. In step 1, hydrosulfide, `[SH-]`, adds to the exocyclic double bond at the carbon bearing the two methyl groups. Hydrolysis then opens the oxazolone, giving **X**, N-acetyl-DL-penicillamine:

`CC(=O)NC(C(=O)O)C(C)(C)S`

The net reaction is

$$\mathrm{U} + \mathrm{H_2S} + \mathrm{H_2O} \longrightarrow \mathrm{X}.$$

Hot aqueous hydrochloric acid hydrolyzes the acetyl protecting group. Calling the resulting racemic penicillamine **P**, `CC(C)(S)C(N)C(=O)O`, the neutral-parent balance is

$$\mathrm{X} + \mathrm{H_2O} \longrightarrow \mathrm{P} + \mathrm{CH_3COOH}.$$

The amino and thiol groups of **P** then condense with acetone, propan-2-one, `CC(=O)C`:

$$\mathrm{P} + (\mathrm{CH_3})_2\mathrm{CO} \longrightarrow \mathrm{B} + \mathrm{H_2O}.$$

The resulting five-membered ring has the sequence

$$\mathrm{S} - \text{acetone-derived carbon} - \mathrm{N} - \text{carboxyl-bearing carbon} - \text{gem-dimethyl carbon}.$$

Consequently, **B** is racemic 2,2,5,5-tetramethyl-1,3-thiazolidine-4-carboxylic acid. The acetone-derived carbon is not stereogenic because it bears two identical methyl groups.

Formation and resolution of C. Formic acid activated by acetic anhydride formylates the secondary ring nitrogen:

$$\mathrm{B} + \mathrm{HCOOH} + (\mathrm{CH_3CO})_2\mathrm{O} \longrightarrow \mathrm{C} + 2\,\mathrm{CH_3COOH}.$$

At this stage **C** is racemic. Brucine forms diastereomeric salts with its two enantiomers, allowing physical separation. The subsequent dilute-acid treatment releases **(+)-C**.

The sign of optical rotation does **not** determine an R/S descriptor. The required configuration follows from the synthesis: this carboxyl-bearing stereocenter becomes the S carboxyl-bearing center of Penicillin VK. Accordingly, **(+)-C** has configuration $4S$.

Formation of D. Step 3 hydrolyzes both the formamide and the acetone-derived N,S-acetal:

$$\mathrm{C} + 2\,\mathrm{H_2O} + \mathrm{HCl} \longrightarrow \mathrm{D}\cdot\mathrm{HCl} + (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{HCOOH}.$$

Thus **D** is (S)-penicillamine, obtained under these conditions as its hydrochloride. Its stereogenic carbon retains its configuration.

Formation of E. Let **G** denote the aldehyde supplied in the scheme: tert-butyl $(2S)$-2-(1,3-dioxoisoindolin-2-yl)-3-oxopropanoate:

`CC(C)(C)OC(=O)[C@@H](N1C(=O)c2ccccc2C1=O)C=O`

The amine of **D** condenses with the aldehyde, and intramolecular thiol addition closes a five-membered thiazolidine ring. Sodium acetate, `CC(=O)[O-].[Na+]`, enables condensation of the hydrochloride salt. A balanced net equation is

$$\mathrm{D}\cdot\mathrm{HCl} + \mathrm{G} + \mathrm{CH_3COONa} \longrightarrow \mathrm{E} + \mathrm{H_2O} + \mathrm{CH_3COOH} + \mathrm{NaCl}.$$

Here sodium chloride is `[Na+].[Cl-]`.

In **E**:

- The penicillamine stereocenter becomes thiazolidine C_4, with configuration S.
- The former aldehyde carbon becomes the new thiazolidine C_2, with configuration R for the product carried through the shown synthesis.
- The external phthalimido-bearing carbon has configuration R.

The last assignment involves a **change of descriptor without inversion**. In **G**, the ester carbon outranks the aldehyde carbon because their next-layer atoms are respectively $(\mathrm{O},\mathrm{O},\mathrm{O})$ and $(\mathrm{O},\mathrm{O},\mathrm{H})$. After cyclization, the former aldehyde carbon is bonded to sulfur, nitrogen and hydrogen. That branch now outranks the ester branch, changing the retained stereocenter's descriptor from S to R.

Removal of the phthaloyl group. Let $\mathrm{Q}\cdot\mathrm{HCl}$ denote the amino ester hydrochloride drawn after step 4: the hydrochloride of $(2R,4S)$-2-[(1R)-1-amino-2-tert-butoxy-2-oxoethyl]-5,5-dimethyl-1,3-thiazolidine-4-carboxylic acid:

`CC(C)(C)OC(=O)[C@@H]([NH3+])[C@H]1SC(C)(C)[C@H](C(=O)O)N1.[Cl-]`

Hydrazine removes the phthaloyl group, producing phthalhydrazide, `O=C1NNC(=O)c2ccccc21`, with formula $\mathrm{C_8H_6N_2O_2}$. Including hydrochloride formation,

$$\mathrm{E} + \mathrm{N_2H_4} + \mathrm{HCl} \longrightarrow \mathrm{Q}\cdot\mathrm{HCl} + \mathrm{C_8H_6N_2O_2}.$$

The tert-butyl ester remains present.

Formation of F. Phenoxyacetyl chloride, `O=C(Cl)COc1ccccc1`, acylates the newly exposed amino group. Triethylamine, `CCN(CC)CC`, accepts the acid.

Let **R** be the resulting side-chain tert-butyl ester of penicilloic acid V:

`CC(C)(C)OC(=O)[C@@H](NC(=O)COc1ccccc1)[C@H]1SC(C)(C)[C@H](C(=O)O)N1`

Accounting for the initial hydrochloride and the acid generated during acylation,

$$\mathrm{Q \cdot HCl + PhOCH_2COCl + 2\,Et_3N \longrightarrow R + 2\,Et_3NHCl.}$$

Triethylammonium chloride is `CC[NH+](CC)CC.[Cl-]`.

Concentrated hydrochloric acid removes the tert-butyl ester; pyridine, `n1ccccc1`, provides the subsequent basic work-up. Written as net ester hydrolysis,

$$\mathrm{R + H_2O \longrightarrow F + (CH_3)_3COH.}$$

The alcohol in this balance is tert-butanol, `CC(C)(C)O`. **F** therefore contains two free carboxylic acid groups, a free thiazolidine nitrogen, and the installed phenoxyacetamido side chain.

Precise wedge–dash descriptions for the answer sheet:

- **A and B:** show racemic structures, using unspecified stereobonds or depicting both enantiomers.
- **(+)-C:** retain the orientation of the drawn racemic **C**. Make the bond from its stereogenic ring carbon to the right-hand carboxyl group a **hashed wedge**, with the corresponding hydrogen toward the viewer. This gives $4S$.
- **D:** draw the backbone with the gem-dimethyl thiol-bearing carbon to the left and the carboxyl carbon to the right. Draw the amino group below the stereocenter on a **hashed wedge**, with hydrogen toward the viewer. This gives $2S$.
- **E and F:** use the orientation of the amino ester shown after step 4. Keep the ring C_4–carboxyl bond as a **solid wedge**, the ring C_2–hydrogen bond as a **solid wedge**, and the external stereocenter's bond to its nitrogen substituent as a **hashed wedge**. In **E**, that nitrogen belongs to the phthalimide group; in **F**, it belongs to the phenoxyacetamido group. **E** has the tert-butyl ester, whereas **F** has the corresponding free carboxylic acid.

6.5. Role of acetone

Acetone, `CC(=O)C`, acts as an **electrophile**.

Its carbonyl carbon accepts nucleophilic attack from the amino group. Condensation and intramolecular sulfur attack then produce the cyclic N,S-acetal. The carbonyl carbon of acetone becomes the ring carbon between nitrogen and sulfur, retaining both methyl groups.

Thus the correct choice is **c)**.

6.6. Role of DCC

DCC is N,N'-dicyclohexylcarbodiimide:

`C1CCC(CC1)N=C=NC2CCCCC2`

It acts as a **coupling reagent**, activating the side-chain carboxyl group of **F** for intramolecular attack by the thiazolidine nitrogen. Formation of this amide bond closes the four-membered β-lactam ring.

DCC is consumed, forming N,N'-dicyclohexylurea, **DCU**:

`O=C(NC1CCCCC1)NC2CCCCC2`

Including potassium hydroxide, `[K+].[OH-]`, the overall atom-balanced reaction is

$$\mathrm{C_{16}H_{20}N_2O_6S + KOH + C_{13}H_{22}N_2 \longrightarrow C_{16}H_{17}KN_2O_5S + C_{13}H_{24}N_2O + H_2O.}$$

The organic reactants are **F** and DCC; the organic products are **Penicillin VK** and DCU. The carboxyl group not incorporated into the β-lactam remains as the potassium carboxylate.

Thus the correct choice is **c)**.

The solution was checked against the official solution.

Problem 7: SABIC

The Saudi Basic Industries Corporation (SABIC) was established in the mid-1970s as part of Saudi Arabia's plan to diversify its economy. Today, SABIC is a global chemical giant, producing 69 million tons of products annually.

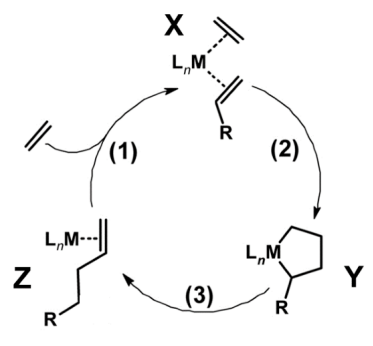
Part A

SABIC's own unique ethene oligomerization technology (oligomers are polymers with few monomer units) produces linear alpha olefins (1-alkenes), which are used in numerous industrial applications.

Linear alpha olefins are produced by catalytic oligomerization of ethene, resulting in a range of chain lengths with a distribution. Different catalysts can yield various distributions of products.

In the geometric or Schulz–Flory distribution, each oligomer fraction is related to the previous fraction by the equation, $T_{n+1} = \alpha T_n$, where T_n represents the molar amount of the oligomer with n ethene units, and α is a constant called the probability of chain propagation. Ethene, the monomer is not a member of the series ($n \geq 2$).

One catalytic oligomerization process can be described by a relatively simple mechanism:



Although this mechanism is not a classical chain reaction because the final product is not produced within the cycle, the usual kinetic treatment of chain reactions can be applied to it. The three processes shown **(1–3)** are all chain propagation steps. R is lengthened by each cycle.

All three reactions are first order with respect to the chain carriers. For ethene, use an unknown order ρ, to be determined later.

7.1 Write the rate equations for reactions **1–3** using k_1, k_2, and k_3 as the corresponding rate constants, which are independent of the carbon chain length. **1 pt**

Chain termination step, producing the oligomers, is a first order reaction competing with reaction **1**.

7.2 Write i) the chemical equation and ii) rate equation of termination. Use k_t as the corresponding rate constant. **2 pt**

7.3 Find the value of ρ which ensures that the product mixture of olefins shows the required ratio of products in accordance with the Schulz–Flory distribution when the reaction is run in a closed system. **Derive** a formula for this case that gives α as the function of rate constants. **4 pt**

Aluminum alkyls are used as co-catalysts in the ethene oligomerization process. It was found that they also catalyzed the Friedel–Crafts alkylation of the aromatic solvents used for the oligomerization.

In a typical oligomerization reaction, an alkylated aromatic compound **Q** was isolated from the complex reaction mixture of ethene oligomerization in toluene as solvent. The alkylated aromatic compound **Q** has the molecular formula $\mathrm{C_{11}H_{16}}$ and its $^1\mathrm{H}$ NMR spectrum contains the following peaks.

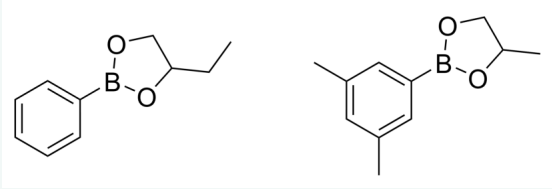
$^1\mathrm{H}$ NMR of **Q**: δ 0.9 (t, 3H); 1.35 (m, 2H); 1.59 (m, 2H); 2.34 (s, 3H), 2.60 (t, 2H); 7.18 (d, 2H); 7.22 (d, 2H).

7.4 Draw the structure of **Q**. **3 pt**

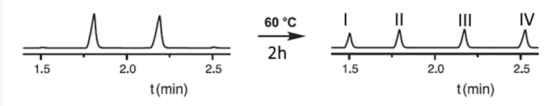
Part B

Vitrimers are adaptive polymers with "reversible" covalent bonds, allowing shape-changing and self-healing under specific conditions. This subtask explores the principles of vitrimer chemistry, an important topic in SABIC's polymer research.

A recently elucidated fast and reversible reaction involving dioxaborolanes can serve as the chemical background for such an adaptable polymer network. The two dioxaborolanes below were prepared by the reaction of phenylboronic acid with 1,2-butanediol and 3,5-dimethylphenylboronic acid with 1,2-propanediol, respectively.



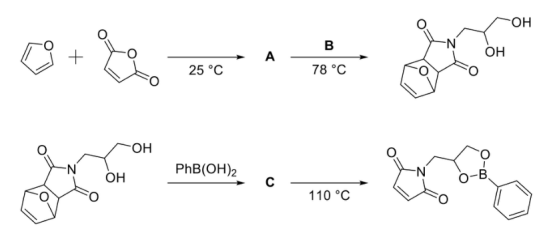
They participate in a model metathesis (exchange) reaction. The two carefully purified compounds were mixed in the absence of solvent and the mixture was kept at $60\ ^\circ\mathrm{C}$ for two hours. Interestingly, the gas chromatograms of the mixture at the start and at the end of the incubation period showed only the peaks below, with equimolar quantities of the components. The peaks in this system separate in a way that correlates with molar mass: compounds with **lower** mass appear at **earlier** elution times.



No catalyst, water, diol or acid was detectable in the mixture.

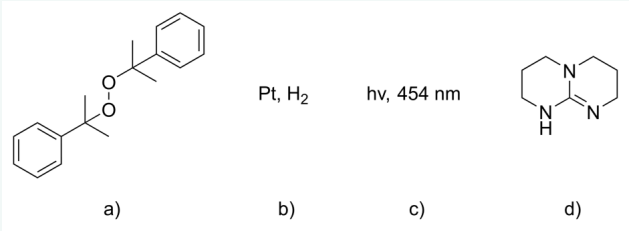
7.5 Draw the compounds associated with peaks I–IV in the chromatogram. **2 pt**

Linking functional units to a polymer chain is known as grafting, and the functional units are referred to as grafting agents. In this case, the dioxaborolane units are linked to the polymer chains by maleimide groups via a radical process, in which one maleimide group is coupling to the polymer chain at a random carbon atom. The scheme below introduces a flexible synthesis route towards the dioxaborolane maleimide grafting agent used in the vitrimers.



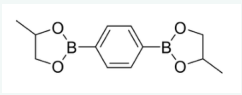
7.6 Draw the structures of **A–C**. **3 pt**

7.7 Select on the answer sheet which reagent(s) and/or condition is/are appropriate for linking the dioxaborolane maleimide units to **polyethylene**. **1 pt**



The vitrimer was prepared as follows:

- Polyethylene is grafted with dioxaborolane maleimide. Assume no side reactions between the dioxaborolane maleimide compounds.
- The reagents are removed from the macromolecules.
- Propanediol functionalized bis-dioxaborolane is added to enable crosslinking.



- The mixture is carefully heated for metathesis (exchange) reaction to take place.

To determine the extent of grafting and crosslinking in the vitrimer, infrared (IR) spectroscopy was used at room temperature where the metathesis reaction is extremely slow. Assume a homogeneous vitrimer.

- All of the small molecules are removed from the polymer.
- The IR spectrum of a thin polymer film is measured.
- IR spectrum contains absorption peaks that correspond to specific functional groups.
- The Beer–Lambert law can be used to quantify the concentration of these functional groups.

The provided data table gives the wavelengths, corresponding molar (related to the specified functional groups) absorption coefficients for relevant characteristic peaks together with the absorbances of the vitrimer sample.

Vibration wavenumber, with the functional group indicated	Molar absorption coefficient, ϵ $(\mathrm{dm^3\,mol^{-1}\,\mu m^{-1}})$	Sample absorbance at this wave number, A
Imide group band at $1710\ \mathrm{cm^{-1}}$	2.67	0.451
Monosubstituted benzene ring band at $1600\ \mathrm{cm^{-1}}$	0.28	0.022
Disubstituted benzene ring band at $1520\ \mathrm{cm^{-1}}$	0.68	0.042
$\mathrm{CH_2}$ groups of polyethylene, band at $1470\ \mathrm{cm^{-1}}$	0.021	0.904

7.8 Calculate the grafting density (X_g) of polyethylene based on the measurements. That is the ratio of the grafted groups over the ethylene units. **3 pt**

7.9 Calculate the percentage of the grafted groups that are **not** part of a crosslink (p_{nc}). **4 pt**

Official English text of the problem.

Answers

- **7.1**

$$\boxed{v_1 = k_1[Z][\mathrm{C_2H_4}]^{\rho}, \qquad v_2 = k_2[X], \qquad v_3 = k_3[Y].}$$

- **7.2**

$$\boxed{\mathrm{Z} \longrightarrow \mathrm{L}_n\mathrm{M} + \mathrm{CH_2{=}CHCH_2CH_2R}}, \qquad \boxed{v_t = k_t[Z].}$$

The released product is a linear terminal alkene, generic SMILES `C=CCC[*]`, where * represents R.

- **7.3**

$$\boxed{\rho = 0, \qquad \alpha = \frac{k_1}{k_1 + k_t}.}$$

- **7.4** **Q** is **1-butyl-4-methylbenzene**, also called p-n**-butyltoluene**: `CCCCc1ccc(C)cc1`.
- **7.5** The compounds, in increasing elution time, are:

I: 4-methyl-2-phenyl-1,3,2-dioxaborolane: `CC1COB(c2ccccc2)O1`.

II: 4-ethyl-2-phenyl-1,3,2-dioxaborolane: `CCC1COB(c2ccccc2)O1`.

III: 2-(3,5-dimethylphenyl)-4-methyl-1,3,2-dioxaborolane: `CC1COB(c2cc(C)cc(C)c2)O1`.

IV: 2-(3,5-dimethylphenyl)-4-ethyl-1,3,2-dioxaborolane: `CCC1COB(c2cc(C)cc(C)c2)O1`.

- **7.6**

A: The furan–maleic anhydride Diels–Alder adduct, represented as **exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride**: `O=C1OC(=O)[C@H]2[C@@H]1[C@@H]1C=C[C@H]2O1`.

B: 3-Aminopropane-1,2-diol: `NCC(O)CO`.

C: Furan-protected N-[(2-phenyl-1,3,2-dioxaborolan-4-yl)methyl]maleimide, retaining the bicyclic core of A: `O=C1N(CC2COB(c3ccccc3)O2)C(=O)[C@H]2[C@@H]1[C@@H]1C=C[C@H]2O1`.

- **7.7** Select **a only**, **dicumyl peroxide**: `CC(C)(OOC(C)(C)c1ccccc1)c1ccccc1`.
- **7.8**

$$\boxed{X_g \approx 7.8 \times 10^{-3} = 0.78\%.}$$

- **7.9**

$$\boxed{p_{nc} \approx 66\%}$$

(the nominal calculation gives 66.2%).

Solution

7.1 — Propagation rate equations

Ethene, SMILES `C=C`, enters in reaction 1, where it reacts with chain carrier Z. Reactions 2 and 3 convert X into Y and Y into Z, respectively, without consuming additional free ethene.

Consequently,

$$v_1 = k_1[Z][\mathrm{C_2H_4}]^{\rho}, \qquad v_2 = k_2[X], \qquad v_3 = k_3[Y].$$

For rates expressed in $\mathrm{mol\,dm^{-3}\,s^{-1}}$, k_2 and k_3 have units $\mathrm{s^{-1}}$, while k_1 has units

$$(\mathrm{mol\,dm^{-3}})^{-\rho}\mathrm{s^{-1}}.$$

7.2 — Termination

Termination competes with ethene capture by Z. It therefore releases the terminal alkene already coordinated to the metal:

$$\mathrm{Z} \xrightarrow{k_t} \mathrm{L_nM} + \mathrm{CH_2{=}CHCH_2CH_2R}.$$

This is dissociation: no atoms are added or removed. The released linear terminal alkene has generic SMILES `C=CCC[*]`, with `*` representing R.

In Z, the alkene is coordinated through its double bond, conventionally described as η^2 coordination. Ordinary molecular SMILES does not show this coordination adequately, and the unspecified metal–ligand fragment $\mathrm{L_nM}$ has no unique molecular SMILES.

Since termination is first order,

$$v_t = k_t[Z],$$

where k_t has units $\mathrm{s^{-1}}$.

7.3 — Condition for the Schulz–Flory distribution

At each visit to Z, a chain can either propagate through reaction 1 or terminate. Its probability of propagation is therefore

$$\alpha = \frac{v_1}{v_1 + v_t} = \frac{k_1[\mathrm{C_2H_4}]^{\rho}}{k_1[\mathrm{C_2H_4}]^{\rho} + k_t}.$$

If this probability is constant, producing an oligomer with one additional ethene unit requires one additional successful propagation. Thus,

$$T_{n+1} = \alpha T_n,$$

and, starting with the smallest oligomer at $n = 2$,

$$T_n = T_2\alpha^{n-2}.$$

In a closed system, ethene concentration decreases as the reaction proceeds. For positive propagation and termination rate constants, the branching probability above is independent of this changing concentration only when

$$\boxed{\rho = 0}.$$

It then becomes

$$\boxed{\alpha = \frac{k_1}{k_1 + k_t}}.$$

The constants k_2 and k_3 determine how quickly the chain passes through X and Y. They do not affect the propagation-versus-termination choice, because neither of those intermediates has a competing termination step in the given mechanism.

7.4 — Identification of Q

For $\mathrm{C_{11}H_{16}}$, the degree of unsaturation is

$$\mathrm{DBE} = \frac{2(11) + 2 - 16}{2} = 4,$$

consistent with one benzene ring.

The NMR assignments are:

Signal	Assignment
$\delta 0.9$, triplet, 3H	Terminal methyl of an n-butyl group
$\delta 1.35$, multiplet, 2H	Butyl methylene next to the terminal methyl
$\delta 1.59$, multiplet, 2H	Middle methylene nearer the aromatic ring
$\delta 2.34$, singlet, 3H	Methyl directly attached to the aromatic ring
$\delta 2.60$, triplet, 2H	Benzylic methylene of the n-butyl group
$\delta 7.18$ and 7.22, two doublets, 2H each	Two equivalent pairs of aromatic hydrogens in a para-disubstituted ring

Therefore, draw a benzene ring bearing methyl and straight-chain butyl groups at opposite positions:

$$\boxed{\text{Q = 1-butyl-4-methylbenzene}}$$

SMILES: `CCCCc1ccc(C)cc1`.

7.5 — Assignment of chromatographic peaks

The exchange reaction produces all four combinations of the two arylboron groups and the two diol residues. Each product retains a five-membered dioxaborolane ring.

Peak	Aryl group attached to boron	Diol-derived substituent on the ring	Molecular formula
I	Phenyl	Methyl	$\mathrm{C_9H_{11}BO_2}$
II	Phenyl	Ethyl	$\mathrm{C_{10}H_{13}BO_2}$
III	3,5-Dimethylphenyl	Methyl	$\mathrm{C_{11}H_{15}BO_2}$
IV	3,5-Dimethylphenyl	Ethyl	$\mathrm{C_{12}H_{17}BO_2}$

Their names and SMILES are given in **Answers 7.5**. To draw each structure, place the stated aryl group on boron and the methyl or ethyl substituent on one carbon of the five-membered ring.

Successive formulas in the table differ by $\mathrm{CH_2}$, so their molar masses increase in exactly the order I–IV. This establishes the elution order using the problem's stated mass–retention relationship.

The starting materials are II and III; exchange produces I and IV:

$$\mathrm{II} + \mathrm{III} \rightleftharpoons \mathrm{I} + \mathrm{IV}.$$

No water, free diol, or free acid is required in this net exchange.

The configurations of the diol-derived stereocentres are not specified in the question; they are therefore left unspecified in the SMILES.

7.6 — Structures A–C

A: Diels–Alder protection. Furan, `c1ccoc1`, reacts as the diene with maleic anhydride, `O=C1OC(=O)C=C1`. The cycloaddition gives the oxygen-bridged bicyclic anhydride A:

$$\mathrm{C_4H_4O} + \mathrm{C_4H_2O_3} \longrightarrow \mathrm{C_8H_6O_4}.$$

Draw the bicyclic skeleton shown in the subsequent protected imide, but with the imide nitrogen replaced by the anhydride oxygen. Retain the oxygen bridge, the remaining carbon–carbon double bond, and the cis relationship inherited from maleic anhydride.

The exo representation used here is:

`O=C1OC(=O)[C@H]2[C@@H]1[C@@H]1C=C[C@H]2O1`.

B: Introduction of the amino diol. The product shown after the $78\ ^\circ\mathrm{C}$ step has an imide nitrogen bearing the side chain $-\mathrm{CH_2CH(OH)CH_2OH}$. Therefore B must be **3-aminopropane-1,2-diol**, `NCC(O)CO`.

Its amino group opens the anhydride; subsequent dehydration forms the imide:

$$\mathrm{C_8H_6O_4} + \mathrm{C_3H_9NO_2} \longrightarrow \mathrm{C_{11}H_{13}NO_5} + \mathrm{H_2O}.$$

The protected hydroxy imide is **furan-protected N-(2,3-dihydroxypropyl)maleimide**:

`O=C1N(CC(O)CO)C(=O)[C@H]2[C@@H]1[C@@H]1C=C[C@H]2O1`.

The coproduct is water, `O`.

C: Formation of the cyclic boronic ester. Phenylboronic acid, `OB(O)c1ccccc1`, condenses with the two adjacent hydroxyl groups, eliminating two molecules of water:

$$\mathrm{C_{11}H_{13}NO_5} + \mathrm{C_6H_7BO_2} \longrightarrow \mathrm{C_{17}H_{16}BNO_5} + 2\,\mathrm{H_2O}.$$

Thus C is **furan-protected N-[(2-phenyl-1,3,2-dioxaborolan-4-yl)methyl]maleimide**:

`O=C1N(CC2COB(c3ccccc3)O2)C(=O)[C@H]2[C@@H]1[C@@H]1C=C[C@H]2O1`.

To draw C, leave the protected imide unchanged and join its two side-chain oxygen atoms to a common boron atom bearing phenyl. This closes the five-membered dioxaborolane ring.

Finally, heating to $110\ ^\circ\mathrm{C}$ causes a retro-Diels–Alder reaction:

$$\mathrm{C_{17}H_{16}BNO_5} \longrightarrow \mathrm{C_{13}H_{12}BNO_4} + \mathrm{C_4H_4O}.$$

The products are furan and the required grafting agent, **N-[(2-phenyl-1,3,2-dioxaborolan-4-yl)methyl]maleimide**:

`O=C1N(CC2COB(c3ccccc3)O2)C(=O)C=C1`.

7.7 — Radical grafting onto polyethylene

Select **a only**.

Dicumyl peroxide, `CC(C)(OOC(C)(C)c1ccccc1)c1ccccc1`, undergoes homolytic cleavage of its peroxide bond on heating. The resulting radicals can abstract hydrogen from polyethylene, generating a polymer radical. Addition of that radical across the maleimide double bond creates the bond connecting the grafting agent to the polymer.

The other choices do not supply the required grafting process:

- **b:** Platinum, `[Pt]`, with dihydrogen, `[H][H]`, provides hydrogenation conditions.
- **c:** Light at $454\ \mathrm{nm}$, without a suitable photoinitiating system, does not provide the required radical initiation.
- **d:** The bicyclic guanidine base **TBD**, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, `C1CN2CCCN=C2NC1`, is not an appropriate initiator for this radical grafting.

7.8 — Grafting density

The Beer–Lambert law is

$$A = \epsilon c \ell,$$

where c is in $\mathrm{mol\,dm^{-3}}$ and film thickness ℓ is in $\mu\mathrm{m}$. Consequently, $A/\epsilon = c\ell$, and the common thickness cancels from concentration ratios.

Each graft contains **one imide group**. The coefficient is specified per imide group, so its two carbonyl groups must not be counted separately.

For the grafts,

$$c_g\ell = \frac{0.451}{2.67} = 0.168914\ \mathrm{mol\,dm^{-3}}\,\mu\mathrm{m}.$$

For polyethylene methylene groups,

$$c_{\mathrm{CH_2}}\ell = \frac{0.904}{0.021} = 43.0476\ \mathrm{mol\,dm^{-3}}\,\mu\mathrm{m}.$$

Each ethylene repeat contains two backbone carbon atoms, represented by the polyethylene repeat fragment `[*]CC[*]`. Using two methylene groups per repeat,

$$X_g = \frac{c_g}{c_{\mathrm{CH_2}}/2} = \frac{2(0.451/2.67)}{0.904/0.021} = 0.00784777.$$

Thus,

$$\boxed{X_g \approx 7.8 \times 10^{-3} = 0.78\%}.$$

The small correction for conversion of one backbone methylene into a methine per graft gives

$$X_g = \frac{2c_g}{c_{\mathrm{CH_2}} + c_g} = 0.00781709,$$

which rounds to the same result.

7.9 — Grafts that are not part of a crosslink

The added crosslinker is **1,4-bis(4-methyl-1,3,2-dioxaborolan-2-yl)benzene**:

`CC1COB(c2ccc(B3OCC(C)O3)cc2)O1`.

A retained crosslinker can be attached to either **one graft** or **two grafts**. Only the latter forms a bridge between grafts. Crosslinkers attached to no grafts are small molecules and have been removed.

Let:

- g: total concentration of grafts, measured through imide groups;
- m: concentration of monosubstituted benzene rings;
- d: concentration of disubstituted benzene rings;
- s: concentration of crosslinker molecules attached to one graft;
- b: concentration of crosslinker molecules attached to two grafts.

Each remaining monosubstituted benzene ring belongs to an original phenylboronate attached to one graft. Each retained disubstituted ring belongs to one crosslinker molecule. Therefore,

$$g = m + s + 2b, \qquad d = s + b.$$

Solving,

$$b = g - m - d, \qquad s = 2d - g + m.$$

The non-crosslinked grafts comprise those retaining their original phenylboronate and those attached to a singly attached crosslinker:

$$g_{nc} = m + s = 2m + 2d - g.$$

The measured quantities are

$$\begin{aligned} g\ell &= \frac{0.451}{2.67} = 0.168914, \\ m\ell &= \frac{0.022}{0.28} = 0.0785714, \\ d\ell &= \frac{0.042}{0.68} = 0.0617647, \end{aligned}$$

all in $\mathrm{mol\,dm^{-3}}\ \mu\mathrm{m}$.

These give

$$b\ell = 0.0285777, \qquad s\ell = 0.0331870.$$

Hence,

$$\begin{aligned} p_{nc} &= 100\frac{m+s}{g} \\ &= 100\left[\frac{2(0.022/0.28) + 2(0.042/0.68)}{0.451/2.67} - 1\right] \\ &= 66.16\ldots\,\%. \end{aligned}$$

Therefore,

$$\boxed{p_{nc} \approx 66\%}.$$

Counting only the monosubstituted benzene groups would miss the grafts bearing singly attached crosslinker molecules.

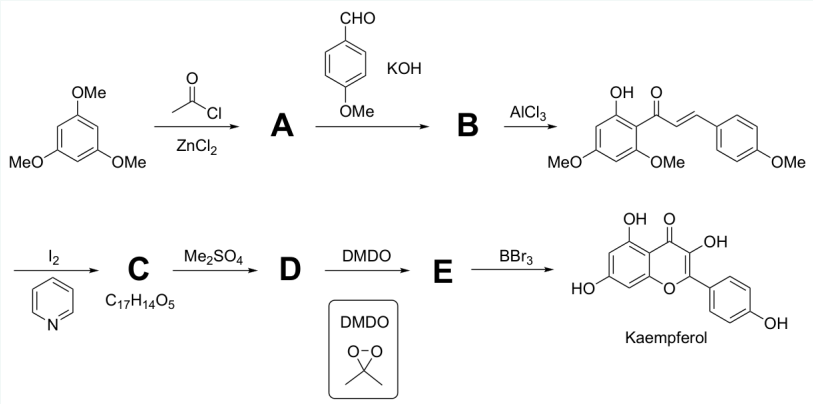
The solution was checked against the official solution.

Problem 8: Safflower

In Saudi culture, safflower drink is a traditional remedy used for its calming effects.



One ingredient with health benefits is kaempferol. The following scheme shows its total synthesis.

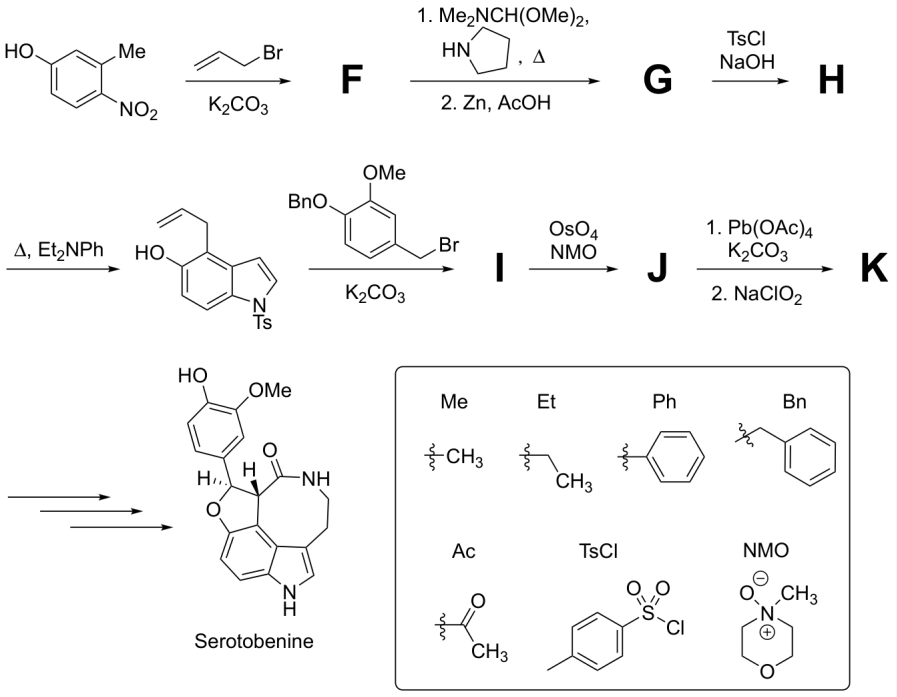


Hints:

- **C** has a tricyclic system. Also, it has the same number of hydroxyl groups as the compound preceding it.
- The step **C** to **D** is necessary to avoid any unwanted reactivity with DMDO.
- DMDO is a hydroxylating agent.

8.1. Draw the structures of compounds A–E. 15 pt

A unique pentacyclic indole alkaloid, serotobenine found in safflower has antimicrobial properties. Its total synthesis is shown below:

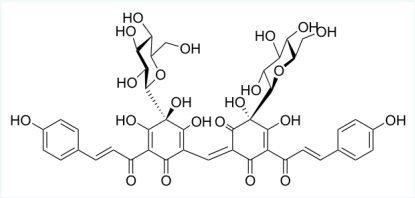


Hints:

- **G** is a bicyclic compound with one of the rings being a heterocycle.
- **H** isomerizes upon heating in the presence of the amine base.
- **K** is a product of an oxidative cleavage of the newly formed functional group in **J**. **K** has a $^1\mathrm{H}$ NMR signal at 12 ppm.

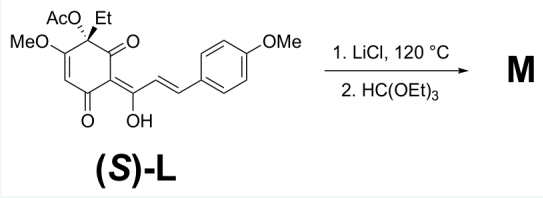
8.2. Draw the structures of compounds F–K. 18 pt

Carthamin gives safflower its red color.



Carthamin

In the total synthesis of carthamin the assembly was tested on a model substrate **L**. Note that **M** resembles carthamin's core structure.



8.3. Draw the structure of compound M including its stereochemistry. (Hint: In methanol-d_4 **L** has 11 and **M** has 10 distinct proton signals in their $^1\mathrm{H}$ NMR spectra). 5 pt

Official English text of the problem.

Answers

8.1.

- **A — 1-(2,4,6-Trimethoxyphenyl)ethan-1-one**, or 2,4,6-trimethoxyacetophenone.
  SMILES: `CC(=O)c1c(OC)cc(OC)cc1OC`
- **B — (2E)-3-(4-Methoxyphenyl)-1-(2,4,6-trimethoxyphenyl)prop-2-en-1-one.**
  SMILES: `COc1ccc(/C=C/C(=O)c2c(OC)cc(OC)cc2OC)cc1`
- **C — 5-Hydroxy-7,4′-dimethoxyflavone.**
  SMILES: `O=c1cc(-c2ccc(OC)cc2)oc2cc(OC)cc(O)c12`

- **D — 5,7,4′-Trimethoxyflavone.**
  SMILES: `O=c1cc(-c2ccc(OC)cc2)oc2cc(OC)cc(OC)c12`
- **E — 3-Hydroxy-5,7,4′-trimethoxyflavone**, or kaempferol 5,7,4′-trimethyl ether.
  SMILES: `O=c1c(O)c(-c2ccc(OC)cc2)oc2cc(OC)cc(OC)c12`

8.2.

- **F — Allyl 3-methyl-4-nitrophenyl ether.**
  SMILES: `C=CCOc1cc(C)c([N+](=O)[O-])cc1`
- **G — 5-(Allyloxy)-1H-indole.**
  SMILES: `C=CCOc1ccc2[nH]ccc2c1`
- **H — 5-(Allyloxy)-1-tosyl-1H-indole.**
  SMILES: `C=CCOc1ccc2n(S(=O)(=O)c3ccc(C)cc3)ccc2c1`
- **I — 4-Allyl-5-[(4-benzyloxy-3-methoxybenzyl)oxy]-1-tosyl-1H-indole.**
  SMILES: `C=CCc1c(OCc2cc(OC)c(OCc3ccccc3)cc2)ccc2n(S(=O)(=O)c3ccc(C)cc3)ccc12`
- **J — Racemic 3-{5-[(4-benzyloxy-3-methoxybenzyl)oxy]-1-tosyl-1H-indol-4-yl}propane-1,2-diol.**
  SMILES: `OCC(O)Cc1c(OCc2cc(OC)c(OCc3ccccc3)cc2)ccc2n(S(=O)(=O)c3ccc(C)cc3)ccc12`
  The unspecified alcohol stereocentre represents the racemic product.
- **K — 2-{5-[(4-Benzyloxy-3-methoxybenzyl)oxy]-1-tosyl-1H-indol-4-yl}acetic acid.**
  SMILES: `O=C(O)Cc1c(OCc2cc(OC)c(OCc3ccccc3)cc2)ccc2n(S(=O)(=O)c3ccc(C)cc3)ccc12`

8.3.

- **M — The homochiral, methine-linked carthamin-model dimer of enol-O-demethylated (S)-L**, with molecular formula $\mathrm{C_{41}H_{38}O_{14}}$. Both original stereocentres retain their configurations.

One neutral keto–enol tautomer, with both stereocentres **S** in this representation, is specified by:

`CC[C@@]1(OC(C)=O)C(=O)/C(=C(/O)\C=C\c2ccc(OC)cc2)C(=O)/C(=C/C2=C(O)[C@](CC)(OC(C)=O)C(=O)/C(=C(/O)\C=C\c3ccc(OC)cc3)C2=O)C1=O`

To draw it, demethylate the **ring enol ether** of each of two copies of **L**, then connect their originally proton-bearing ring alkene carbons through one methine carbon. Represent the central conjugated segment as $\mathrm{C_{ring}}=\mathrm{CH}-\mathrm{C_{ring}}$, with the adjacent carbonyl/enol arrangement encoded above. Retain both acetoxy groups, both ethyl groups and both aryl methoxy groups.

Solution

8.1. Identification of A–E

A: Friedel–Crafts acylation.
The three unsubstituted positions of the starting 1,3,5-trimethoxybenzene are equivalent. Acetylation introduces an acetyl group at one of them, giving **A**, 2,4,6-trimethoxyacetophenone.

The balanced organic transformation is

$$\mathrm{C_9H_{12}O_3 + CH_3COCl \xrightarrow{ZnCl_2} C_{11}H_{14}O_4 + HCl.}$$

B: Claisen–Schmidt condensation.
Base forms the enolate of **A**, which adds to the aldehyde carbonyl. Dehydration gives the conjugated chalcone **B**, predominantly with the E configuration:

$$\mathrm{C_{11}H_{14}O_4 + C_8H_8O_2 \xrightarrow{KOH} C_{19}H_{20}O_5 + H_2O.}$$

The carbonyl remains attached to the trimethoxyphenyl ring.

C: Cyclization accompanied by another demethylation.
The displayed product of the $\mathrm{AlCl_3}$ step is **(2E)-1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one**:

`COc1ccc(/C=C/C(=O)c2c(O)cc(OC)cc2OC)cc1`

Its ortho phenolic oxygen becomes the heterocyclic oxygen during oxidative cyclization. The chalcone's carbonyl, α-carbon and β-carbon become flavone C4, C3 and C2, respectively.

Cyclization alone would give a trimethoxyflavone with formula $\mathrm{C_{18}H_{16}O_5}$, containing **no free hydroxyl group**. However, **C** must have formula $\mathrm{C_{17}H_{14}O_5}$ and one hydroxyl group. Therefore, one further methoxy group must be demethylated.

The remaining methoxy group ortho to the carbonyl becomes flavone's **5-hydroxyl group**. Thus **C** is 5-hydroxy-7,4′-dimethoxyflavone. This accounts for its formula and all three rings.

D: Protection of the phenolic hydroxyl group.
Dimethyl sulfate methylates the 5-hydroxyl group, giving **D**, 5,7,4′-trimethoxyflavone. Protection prevents unwanted oxidation of the free phenol during the next step.

E: Hydroxylation at C3.
DMDO introduces the hydroxyl group at flavone C3, giving **E**, 3-hydroxy-5,7,4′-trimethoxyflavone.

The balanced oxygen-transfer equation is

$$\mathrm{C_{18}H_{16}O_5 + C_3H_6O_2 \longrightarrow C_{18}H_{16}O_6 + C_3H_6O.}$$

Here the oxygen donor is **dimethyldioxirane**, `CC1(C)OO1`, and its reduction product is **acetone**, `CC(=O)C`.

Finally, $\mathrm{BBr_3}$ cleaves the three methyl ethers. The existing 3-hydroxyl group remains, producing **kaempferol**, or 3,5,7,4′-tetrahydroxyflavone:

`O=c1c(O)c(-c2ccc(O)cc2)oc2cc(O)cc(O)c12`

8.2. Identification of F–K

F: Phenolic O-allylation.
Potassium carbonate generates the phenoxide, which substitutes bromide from allyl bromide. This gives the allyl ether **F**. The methyl and nitro groups remain unchanged.

G: Leimgruber–Batcho indole synthesis.
The adjacent methyl and nitro groups provide the required ortho-nitrotoluene arrangement.

The acetal/pyrrolidine treatment converts the methyl substituent into an enamine-containing two-carbon side chain. Zinc in acetic acid then reduces the nitro group, enabling intramolecular ring closure and formation of the aromatic indole.

The original nitro-bearing aromatic carbon becomes indole C7a, while the original methyl-bearing aromatic carbon becomes C3a. Consequently, the allyloxy substituent is at **C5**, identifying **G** as 5-(allyloxy)-1H-indole.

H: Indole N-protection.
Tosyl chloride replaces the indole N–H hydrogen with a tosyl group. The oxygen is already protected as an allyl ether, so **H** is the N-tosyl derivative of **G**.

Formation of I: Claisen rearrangement followed by O-benzylation.
Heating **H** causes an aromatic Claisen rearrangement: the oxygen-bound allyl group migrates to the adjacent **C4** position, and the phenolic hydroxyl group is restored.

The depicted rearrangement product is **4-allyl-5-hydroxy-1-tosyl-1H-indole**:

`C=CCc1c(O)ccc2n(S(=O)(=O)c3ccc(C)cc3)ccc12`

Its phenolic oxygen then substitutes bromide from the supplied substituted benzyl bromide. The benzyl ring bears methoxy at position 3 and benzyloxy at position 4, giving **I**.

J: Alkene dihydroxylation.
The $\mathrm{OsO_4}$/NMO system converts the terminal allyl double bond into a vicinal diol. Thus the substituent changes from an allyl group to a 2,3-dihydroxypropyl group:

- In **I**, the side chain is ring–$\mathrm{CH_2CH{=}CH_2}$.
- In **J**, it is ring–$\mathrm{CH_2CH(OH)CH_2OH}$.

Addition is syn. Since the substrate and reagents are achiral and only one stereocentre is created, **J** is racemic.

K: Oxidative cleavage followed by aldehyde oxidation.
Lead tetraacetate cleaves the bond between the two hydroxyl-bearing carbons of **J**. The terminal carbon is removed from the retained side chain, leaving an aldehyde attached through the original benzylic methylene.

Sodium chlorite oxidizes this aldehyde to the carboxylic acid **K**. Therefore, the substituent in **K** is ring–$\mathrm{CH_2CO_2H}$, rather than a carboxyl group directly attached to the ring.

The signal at **12 ppm** is consistent with a carboxylic-acid proton.

8.3. Structure and stereochemistry of M

For this explanation, number each ring of **L** locally from the ethyl/acetoxy-bearing stereocentre as **C1**, proceeding clockwise in the supplied drawing. Then:

- C2 and C4 are carbonyl carbons.
- C3 carries the exocyclic enol side chain.
- The left-hand ring double bond is C5=C6, with methoxy at C6.

Demethylation.
Heating with LiCl cleaves the methyl group from the activated **C6 enol ether**. The aryl methoxy group and the acetoxy group are retained.

The resulting **6-hydroxy analogue of (S)-L**, after protonation, has SMILES:

`CC[C@@]1(OC(C)=O)C(=O)/C(=C(/O)\C=C\c2ccc(OC)cc2)C(=O)C=C1O`

Its formula is $\mathrm{C_{20}H_{20}O_7}$.

Methine-bridge formation.
Triethyl orthoformate supplies one carbon that links C5 of two such units. Elimination of ethanol produces the conjugated methine-linked dimer:

$$\mathrm{2\,C_{20}H_{20}O_7 + HC(OC_2H_5)_3 \longrightarrow C_{41}H_{38}O_{14} + 3\,C_2H_5OH.}$$

In the tautomer specified in the answer:

- The first ring has a C5=CH bond to the bridge and a C6 carbonyl.
- The second ring is singly bonded from C5′ to the bridge and retains C5′=C6′–OH.
- Both original exocyclic enol side chains remain represented as in **L**.
- The central double bond has the Z arrangement encoded in the SMILES.

This produces the same methine-linked, conjugated ring framework found in carthamin.

Stereochemistry.
Neither transformation breaks a bond at either acetoxy/ethyl-bearing stereocentre. Both centres therefore retain their absolute configurations. In the particular tautomer used in the answer, both are **S**. The original E side-chain alkene geometries are also retained.

Check against the NMR hint.
Exchangeable hydroxyl protons are excluded in methanol-d_4. The ethyl methylene hydrogens are diastereotopic because of the neighbouring stereocentre.

For **M**, rapid keto–enol exchange makes the corresponding environments of its two halves equivalent on the NMR timescale.

Proton environment	Signals in L	Signals in M
Para-disubstituted phenyl ring	2	2
Side-chain alkene hydrogens	2	2
Aryl methoxy group	1	1
Ring enol-ether methoxy group	1	0
Acetoxy methyl group	1	1
Ethyl methyl group	1	1
Diastereotopic ethyl methylene hydrogens	2	2
Original ring C5–H	1	0
New bridging methine hydrogen	0	1
Total	**11**	**10**

The predicted counts agree with both values supplied in the problem.

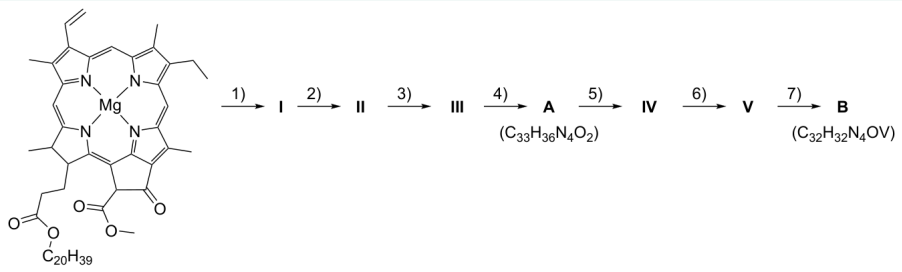
The solution was checked against the official solution.

Problem 9: Porphyrin complexes

Part A. Metals in petroleum

Saudi Arabian petroleum, primarily hydrocarbons, contains elements like vanadium in porphyrin complexes, hinting at its biological origins.

Vanadium complex **B** is presumably formed in petroleum from chlorophyll according to the following scheme:

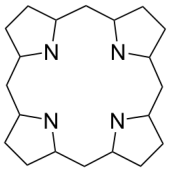
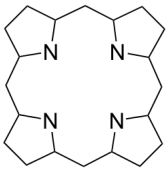


Step	Name
1)	Demetallization
2)	Hydrolysis
3)	Decarbomethoxylation
4)	Reduction
5)	Aromatization
6)	Decarboxylation
7)	Metal chelation

9.1 Assign the molecular formulae **a–e** (given in the answer sheet) to the intermediates **I–V**. **4.0 pt**

a	b	c	d	e
$C_{32}H_{34}N_4$	$C_{55}H_{74}N_4O_5$	$C_{33}H_{34}N_4O_3$	$C_{33}H_{34}N_4O_2$	$C_{35}H_{36}N_4O_5$

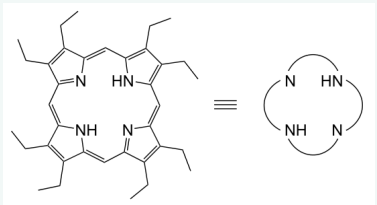
9.2 Draw the structures of intermediate **A** and vanadium complex **B** using the pre-drawn framework of porphyrin. *(If you need a new template to redraw your structure(s), please ask the supervisor.)* **7.0 pt**

	
A ($C_{33}H_{36}N_4O_2$)	**B** ($C_{32}H_{32}N_4OV$)

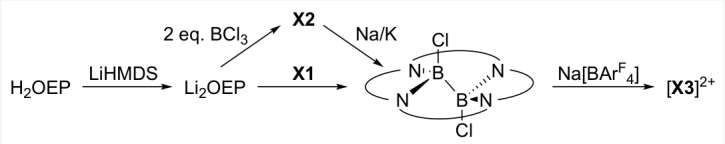
9.3 Indicate the oxidation state of vanadium in **B**. **1.0 pt**

Part B. Porphyrin non-metal complexes

Porphyrins are known to form chelate-type complexes not only with metals but also with some non-metals, for example, with boron and phosphorus. Octaethylporphyrin ($\mathrm{H_2OEP}$) is often used to model natural porphyrins and to study porphyrin complexes. It has the following structure and can be represented as:



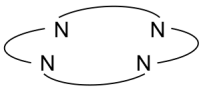
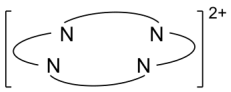
To produce dicationic planar boron porphyrin complex $[\mathrm{X_3}]^{2+}$, either $\mathrm{BCl_3}$ or another binary compound **X1** can be used as a precursor:



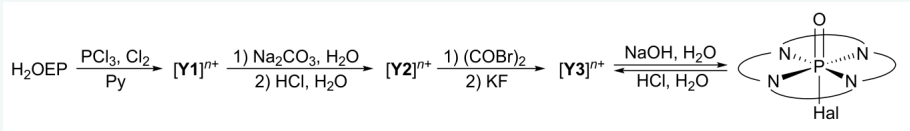
(LiHMDS = $\mathrm{LiN(SiMe_3)_2}$; $\mathrm{Na[BAr^F_4] = Na[B\{(3,5)-(CF_3)_2C_6H_3\}_4]}$)

9.4 Draw the structures of **X1**, intermediate complex **X2** and the product $[\mathrm{X_3}]^{2+}$. **3.0 pt**

9.4 (3.0 pt)

		
X1	**X2**	[**X3**]$^{2+}$

Phosphorus forms porphyrin cationic complexes $[\mathrm{Y_1}]^{n+}$, $[\mathrm{Y_2}]^{n+}$, and $[\mathrm{Y_3}]^{n+}$. The complex $[\mathrm{Y_3}]^{n+}$ has one less plane of symmetry compared to $[\mathrm{Y_1}]^{n+}$ and $[\mathrm{Y_2}]^{n+}$ (ignore ethyl substituents in OEP ligand when considering symmetry). Pyridine (Py) is used here as a basic solvent, "Hal" is one of the halogens: F, Cl, or Br:



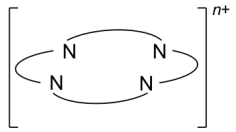
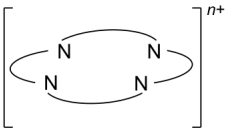
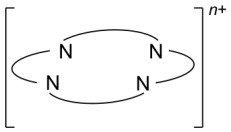
9.5 Indicate: a) the charge "$n+$" of phosphorus porphyrin complexes; b) the number of planes of symmetry $N(\sigma)$ that complex $[\mathrm{Y_1}]^{n+}$ has. **2.0 pt**

9.5 (2.0 pt)

a) $n+$ =	b) $N(\sigma)$ =

9.6 Draw the structures of $[\mathrm{Y_1}]^{n+}$, $[\mathrm{Y_2}]^{n+}$, and $[\mathrm{Y_3}]^{n+}$. **4.0 pt**

9.6 (4.0 pt)

		
$[\mathbf{Y1}]^{n+}$	$[\mathbf{Y2}]^{n+}$	$[\mathbf{Y3}]^{n+}$

Part C. Porphyrin sandwiches

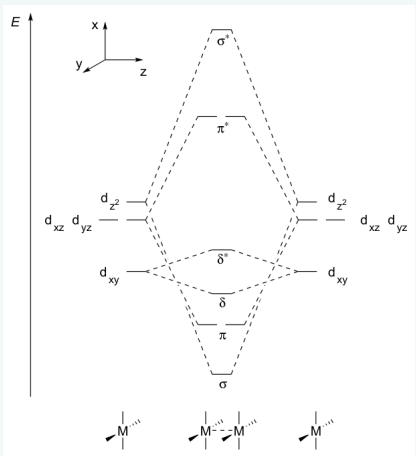
Porphyrin sandwich-type complexes form when there are several porphyrin rings aligned relative to each other. Examples are $\mathrm{Zr(OEP)_2}$, $\mathrm{Eu_2(OEP)_3}$, $\mathrm{Bi_2(OEP)_2Cl_2}$ that have at least 3 planes of symmetry each. Note that the hole size in the OEP ligand is ca. 4.0 Å, and the average metal–N distances in these complexes are $2.4,\ 2.5,\ 2.3$ Å, respectively.

9.7 Suggest the structures of $\mathrm{Zr(OEP)_2}$, $\mathrm{Eu_2(OEP)_3}$, and $\mathrm{Bi_2(OEP)_2Cl_2}$. You may use a simplified representation of the OEP ligand. **3.0 pt**

9.7 (3.0 pt)

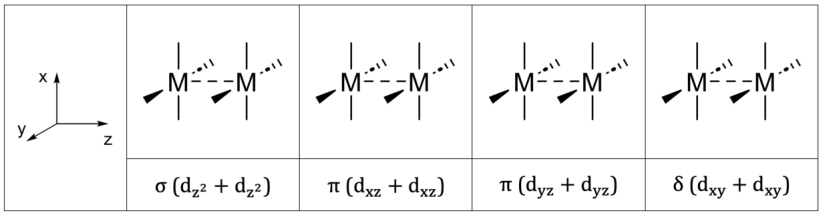
$\mathrm{Zr(OEP)_2}$	$\mathrm{Eu_2(OEP)_3}$	$\mathrm{Bi_2(OEP)_2Cl_2}$

Another type of porphyrin sandwich-type complex is metal–porphyrin dimers with single or multiple metal–metal bonds. For example, $[\mathrm{Ru(OEP)}]_2$ has a Ru–Ru double bond (considering only d-electrons). Below is the molecular orbital diagram for an eclipsed dimer of the type $[\mathrm{M(porphyrin)}]_2$ (interaction between $\mathrm{d}_{x^2-y^2}$ is not considered as these orbitals lie high in energy):



9.8 Draw the $\sigma(\mathrm{d}_{z^2}+\mathrm{d}_{z^2})$, $\pi(\mathrm{d}_{xz}+\mathrm{d}_{xz})$, $\pi(\mathrm{d}_{yz}+\mathrm{d}_{yz})$, and $\delta(\mathrm{d}_{xy}+\mathrm{d}_{xy})$ bonding orbitals according to the specified coordinate system. **4.0 pt**

9.8 (4.0 pt)



9.9 Calculate the metal–metal bond order in the following complexes in eclipsed conformation: $[\mathrm{Mo(OEP)}]_2$, $[\mathrm{Ir(OEP)}]_2$, $[\mathrm{Re(OEP)}]_2{}^+$. **3.0 pt**

$[\mathrm{Mo(OEP)}]_2$	$[\mathrm{Ir(OEP)}]_2$	$[\mathrm{Re(OEP)}]_2{}^+$

The eclipsed conformation is generally preferred for metal–porphyrin dimers with 7, 8, and 9 d-electrons. Otherwise, these complexes are more stable in a staggered conformation, where the porphyrin rings are rotated relative to each other by 45°.

9.10 Select how the splitting (i.e., the energy between antibonding and bonding orbitals) changes for each type of orbital interaction during the conversion of eclipsed conformation into staggered:

a) increases;
b) remains unchanged;
c) decreases (not to zero);
d) decreases to zero.

4.0 pt

9.10 (4.0 pt)

σ/σ^*	π/π^*	δ/δ^*
☐ a ☐ b ☐ c ☐ d	☐ a ☐ b ☐ c ☐ d	☐ a ☐ b ☐ c ☐ d

Official English text of the problem.

Answers

Here L^{2-} denotes the octaethylporphyrinato ligand, OEP^{2-}. Full structural descriptions and SMILES follow in the Solution.

- **9.1:** $\boxed{\mathrm{I}=\mathrm{b},\ \mathrm{II}=\mathrm{e},\ \mathrm{III}=\mathrm{c},\ \mathrm{IV}=\mathrm{d},\ \mathrm{V}=\mathrm{a}}$.
- **9.2: A** is 13^1-deoxopyropheophorbide a: the phytyl ester is hydrolysed, the methoxycarbonyl substituent is removed, and the ring ketone becomes a methylene group. **B** is its aromatized, decarboxylated oxovanadium(IV) complex; the vinyl group remains unchanged.
- **9.3:** $\boxed{+4}$.
- **9.4: X1** is diboron tetrachloride, $\mathrm{Cl_2B{-}BCl_2}$. **X2** is $\mathrm{L(BCl_2)_2}$, with two adjacent N donors per B and no B–B bond. $[\mathrm{X_3}]^{2+}$ is planar $[\mathrm{LB_2}]^{2+}$, retaining a B–B single bond.
- **9.5:** a) $\boxed{n+=1+}$; b) $\boxed{N(\sigma)=5}$.
- **9.6:** $\boxed{[\mathrm{Y_1}]^+=[\mathrm{P(L)Cl_2}]^+}$, $\boxed{[\mathrm{Y_2}]^+=[\mathrm{P(L)(OH)_2}]^+}$, and $\boxed{[\mathrm{Y_3}]^+=[\mathrm{P(L)(OH)F}]^+}$. Each has two mutually trans axial ligands.
- **9.7:** $\mathrm{ZrL_2}$: an eight-coordinate double-decker sandwich. $\mathrm{Eu_2L_3}$: a triple-decker sandwich with one eight-coordinate Eu between each pair of adjacent decks. $\mathrm{Bi_2L_2Cl_2}$: $\mathrm{LBi}(\mu\text{-}\mathrm{Cl})_2\mathrm{BiL}$, with two bridging chlorides.
- **9.8:** Constructive end-on d_{z^2} overlap gives σ; constructive side-on overlap in the xz and yz planes gives the two π orbitals; four-lobe face-to-face d_{xy} overlap gives δ.
- **9.9:** $\boxed{4,\ 1,\ 3.5}$, respectively.
- **9.10:** $\boxed{\sigma/\sigma^*:b;\quad \pi/\pi^*:b;\quad \delta/\delta^*:d}$.

Solution

SMILES below specify connectivity. Dative bonds are written using –>; coordination geometries are described separately. Formal charges appearing in a SMILES representation are not necessarily oxidation states. Stereochemistry not specified by the supplied drawings is left unspecified.

9.1 — Assignment of molecular formulae

The starting chlorophyll has formula $\mathrm{C_{55}H_{72}MgN_4O_5}$.

Intermediate	Formula	Choice	Identification
I	$\mathrm{C_{55}H_{74}N_4O_5}$	**b**	Pheophytin a
II	$\mathrm{C_{35}H_{36}N_4O_5}$	**e**	Pheophorbide a
III	$\mathrm{C_{33}H_{34}N_4O_3}$	**c**	Pyropheophorbide a
IV	$\mathrm{C_{33}H_{34}N_4O_2}$	**d**	Aromatized A
V	$\mathrm{C_{32}H_{34}N_4}$	**a**	Decarboxylated IV, the metal-free ligand of B

The atom balances explain every assignment:

1. **Demetallization:** replace the central $\mathrm{Mg^{2+}}$ by two N-bound hydrogens.
$$\mathrm{C_{55}H_{72}MgN_4O_5 + 2\,H^+ \longrightarrow C_{55}H_{74}N_4O_5 + Mg^{2+}}$$
2. **Hydrolysis:** cleave the phytyl ester, replacing $\mathrm{-OC_{20}H_{39}}$ by $\mathrm{-OH}$.
$$\mathrm{C_{55}H_{74}N_4O_5 + H_2O \longrightarrow C_{35}H_{36}N_4O_5 + C_{20}H_{40}O}$$
3. **Decarbomethoxylation:** replace the ring's $\mathrm{-CO_2CH_3}$ substituent by H. An atom-balanced hydrolysis/decarboxylation description is
$$\mathrm{C_{35}H_{36}N_4O_5 + H_2O \longrightarrow C_{33}H_{34}N_4O_3 + CO_2 + CH_3OH.}$$
4. **Reduction:** convert the remaining ring ketone into a methylene group.
$$\mathrm{C_{33}H_{34}N_4O_3 + 2\,H_2 \longrightarrow C_{33}H_{36}N_4O_2 + H_2O}$$
5. **Aromatization:** remove two hydrogens from the reduced pyrrole ring.
$$\mathrm{C_{33}H_{36}N_4O_2 \longrightarrow C_{33}H_{34}N_4O_2 + H_2}$$
6. **Decarboxylation:**
$$\mathrm{C_{33}H_{34}N_4O_2 \longrightarrow C_{32}H_{34}N_4 + CO_2}$$
7. **Vanadyl chelation:**
$$\mathrm{C_{32}H_{34}N_4 + VO^{2+} \longrightarrow C_{32}H_{32}N_4OV + 2\,H^+}$$

The $\mathrm{H_2}$ terms in steps 4–5 express the net redox balances; the actual reducing and oxidizing reagents are not specified.

The corresponding structural SMILES are:

- **I, pheophytin a**, using the conventional phytyl connectivity:
`C=CC1=C(C)c2cc3[nH]c(c4c5nc(cc6[nH]c(cc1n2)c(C)c6CC)C(C)=C5C(=O)C4C(=O)OC)C(CCC(=O)OCC=C(C)CCCC(C)CCCC(C)CCCC(C)C)C`
- **II, pheophorbide a:**
`C=CC1=C(C)c2cc3[nH]c(c4c5nc(cc6[nH]c(cc1n2)c(C)c6CC)C(C)=C5C(=O)C4C(=O)OC)C(CCC(=O)O)C3C`
- **III, pyropheophorbide a:**
`C=CC1=C(C)c2cc3[nH]c(c4c5nc(cc6[nH]c(cc1n2)c(C)c6CC)C(C)=C5C(=O)C4)C(CCC(=O)O)C3C`
- **IV, the aromatized derivative of A:**
`C=CC1=C(C)c2cc3[nH]c(c4c5nc(cc6[nH]c(cc1n2)c(C)c6CC)C(C)=C5CC4)c(CCC(=O)O)c3C`
- **V, the decarboxylated derivative of IV:**
`C=CC1=C(C)c2cc3[nH]c(c4c5nc(cc6[nH]c(cc1n2)c(C)c6CC)C(C)=C5CC4)c(CC)c3C`

9.2 — Structures of A and B

A: $\mathrm{13^1}$**-deoxopyropheophorbide a**, $\mathrm{C_{33}H_{36}N_4O_2}$.

SMILES:
`C=CC1=C(C)c2cc3[nH]c(c4c5nc(cc6[nH]c(cc1n2)c(C)c6CC)C(C)=C5CC4)C(CCC(=O)O)C3C`

To draw **A**, retain the orientation and peripheral substitution of the starting chlorophyll, making these changes:

- Remove Mg and place H on the upper-right and lower-left nitrogens, giving a free-base chlorin.
- Change the lower-left propionate ester into $\mathrm{-CH_2CH_2COOH}$.
- Remove the methoxycarbonyl substituent from the fused five-membered ring, replacing it by H.
- Replace that ring's $\mathrm{C{=}O}$ group by $\mathrm{CH_2}$.
- Retain the upper-left vinyl group, the upper-right ethyl group, all four methyl groups, and the saturated bond between the two peripheral carbons of the lower-left pyrrole ring.

The fused five-membered ring consequently contains a $\mathrm{-CH_2-CH_2^-}$ bridge connecting the same two macrocycle positions as in the starting structure.

The formula fixes the extent of reduction: replacing $\mathrm{C{=}O}$ by $\mathrm{CH_2}$ accounts exactly for the change from $\mathrm{C_{33}H_{34}N_4O_3}$ to $\mathrm{C_{33}H_{36}N_4O_2}$. Additional hydrogenation of the vinyl group would give too many hydrogens.

B: the oxovanadium(IV) complex of V, $\mathrm{C_{32}H_{32}N_4OV}$.

SMILES:
`C=CC1=C(C)c2cc3c(C)c(CC)c4c5c6[n]7->[V+2]8(=[O])(<-[n]2c1cc1c(C)c(CC)c(cc7C(C)=C6CC5)[n-]->81)<-[n-]34`

To obtain its drawing from **A**:

1. Introduce a double bond between the two saturated peripheral carbons of the lower-left pyrrole ring, producing the porphyrin conjugation pattern.
2. Replace $\mathrm{-CH_2CH_2COOH}$ by $\mathrm{-CH_2CH_3}$.
3. Remove both inner N–H hydrogens and coordinate all four nitrogens to V.
4. Add a terminal axial oxo ligand, drawn $\mathrm{V{=}O}$.

The coordination geometry is approximately **square pyramidal**: four porphyrin nitrogens form the basal donor set and oxygen occupies the axial position. The peripheral vinyl group remains unchanged.

9.3 — Oxidation state of vanadium

The porphyrinato ligand has charge -2, and the oxo ligand has charge -2. Since **B** is neutral,

$$x - 2 - 2 = 0, \qquad \boxed{x = +4}.$$

Thus the metal is vanadium(IV).

9.4 — Boron complexes

Let L^{2-} denote **octaethylporphyrinato**, whose SMILES is:

`CCC1=C(CC)c2cc3[n-]c(cc4nc(cc5[n-]c(cc1n2)c(CC)c5CC)C(CC)=C4CC)c(CC)c3CC`

The two inner N–H groups are first deprotonated:

$$\mathrm{H_2L} + 2\,\mathrm{LiN(SiMe_3)_2} \longrightarrow \mathrm{Li_2L} + 2\,\mathrm{HN(SiMe_3)_2}.$$

X1 is diboron tetrachloride, $\mathrm{B_2Cl_4}$.

SMILES: `ClB(Cl)B(Cl)Cl`

Draw a B–B single bond, with two terminal chlorides on each B. Its reaction with the dilithium ligand is

$$\mathrm{Li_2L} + \mathrm{B_2Cl_4} \longrightarrow \mathrm{L(BCl)_2} + 2\,\mathrm{LiCl}.$$

This directly gives the B–B-bonded dichloro complex shown in the problem.

X2 is the bis(dichloroboron) octaethylporphyrin complex, $\mathrm{L(BCl_2)_2}$.

SMILES:
`CCC1=C(CC)C2=[N+]3C1=Cc1c(CC)c(CC)c(n1[B-]3(Cl)Cl)C=C1C(CC)=C(CC)C3=[N+]1[B-](Cl)(Cl)n1c(c(CC)c(CC)c1=C3)=C2`

Draw two B centres inside the macrocycle. One binds the two adjacent nitrogens on the left, and the other binds the two adjacent nitrogens on the right. Each B also bears **two chlorides**, giving approximately tetrahedral coordination. **There is no B–B bond in X2.**

Formation and reduction are balanced by

$$\mathrm{Li_2L} + 2\,\mathrm{BCl_3} \longrightarrow \mathrm{L(BCl_2)_2} + 2\,\mathrm{LiCl},$$
$$\mathrm{L(BCl_2)_2} + 2\,\mathrm{M} \longrightarrow \mathrm{L(BCl)_2} + 2\,\mathrm{MCl}, \qquad \mathrm{M = Na\ or\ K}.$$

The latter reaction reduces each B from oxidation state $+3$ to $+2$, removes one chloride from each, and forms the B–B bond.

$[\mathrm{X_3}]^{2+}$ **is the B–B-bonded diboron octaethylporphyrin dication**, $[\mathrm{LB_2}]^{2+}$.

SMILES:
`CCC1=C(CC)C2=[N+]3B4B5n6c(c(CC)c(CC)c6=CC6=[N+]5C(=Cc5c(CC)c(CC)c(n54)C=C13)C(CC)=C6CC)=C2`

Draw the same adjacent N-pair chelation, remove both remaining chlorides, and retain the **B–B single bond**. The two B centres and four N donors are coplanar; each B is three-coordinate.

Writing $\mathrm{W^-}$ for the weakly coordinating borate anion supplied in the problem,

$$\mathrm{L(BCl)_2} + 2\,\mathrm{NaW} \longrightarrow [\mathrm{LB_2}]\mathrm{W_2} + 2\,\mathrm{NaCl}.$$

Chloride abstraction is not a further reduction, so it does not increase the B–B bond order. Charge balance also gives

$$2(+2) + (-2) = +2$$

for the diboron porphyrin dication.

9.5 — Charge and symmetry of the phosphorus complexes

Phosphorus is in oxidation state $+5$. With a dianionic porphyrinato ligand and two singly charged axial ligands,

$$q = +5 - 2 - 1 - 1 = +1.$$

Therefore,

$$\boxed{n+ = 1+}.$$

For **Y1**, the two identical axial chlorides and the idealized unsubstituted porphyrin framework give D_{4h} symmetry. Its mirror planes are:

- the porphyrin plane, σ_h;
- two vertical planes passing through opposite N donors;
- two further vertical planes bisecting those N–P–N directions.

Hence

$$\boxed{N(\sigma) = 1 + 2 + 2 = 5}.$$

9.6 — Phosphorus structures

All three cations contain P coordinated to the four porphyrin nitrogens, with two additional ligands on opposite sides of the porphyrin plane.

Species	Identification	Axial ligands
$[\mathrm{Y_1}]^+$	Dichlorido(octaethylporphyrinato)phosphorus(V)	Cl and Cl
$[\mathrm{Y_2}]^+$	Dihydroxido(octaethylporphyrinato)phosphorus(V)	OH and OH
$[\mathrm{Y_3}]^+$	Fluorido(hydroxido)(octaethylporphyrinato)phosphorus(V)	F and OH

Their SMILES, using covalent, charge-separated representations of the P–N bonds, are:

- $[\mathrm{Y_1}]^+$:
  `CCC1=C(CC)C2=[N+]3C1=Cc1c(CC)c(CC)c4n1[P-]31(Cl)(Cl)n3c(c(CC)c(CC)c3=CC3=[N+]1C(=C4)C(CC)=C3CC)=C2`
- $[\mathrm{Y_2}]^+$:
  `CCC1=C(CC)C2=[N+]3C1=Cc1c(CC)c(CC)c4n1[P-]31(O)(O)n3c(c(CC)c(CC)c3=CC3=[N+]1C(=C4)C(CC)=C3CC)=C2`
- $[\mathrm{Y_3}]^+$:
  `CCC1=C(CC)C2=[N+]3C1=Cc1c(CC)c(CC)c4n1[P-]31(O)(F)n3c(c(CC)c(CC)c3=CC3=[N+]1C(=C4)C(CC)=C3CC)=C2`

The initial oxidative insertion can be balanced as

$$\mathrm{H_2L + PCl_3 + Cl_2 \longrightarrow [P(L)Cl_2]Cl + 2\,HCl.}$$

Pyridine acts as a base and captures the acid.

Hydrolysis replaces the axial chlorides with hydroxido ligands. A net balance including carbonate is

$$\mathrm{[P(L)Cl_2]^+ + Na_2CO_3 + H_2O \longrightarrow [P(L)(OH)_2]^+ + 2\,NaCl + CO_2.}$$

The acid workup establishes the protonated hydroxido form shown as **Y2**.

The decisive information for **Y3** is its reversible conversion, under base, to the neutral oxo–halido complex. Thus **Y3** must retain **one OH group**:

$$\mathrm{[P(L)(OH)Hal]^+ + OH^- \longrightarrow P(L)(O)Hal + H_2O.}$$

Since the last substitution reagent is KF, $\mathrm{Hal = F}$. An overall atom-balanced description of the oxalyl bromide/fluoride sequence is

$$\mathrm{[P(L)(OH)_2]^+ + (COBr)_2 + KF \longrightarrow [P(L)(OH)F]^+ + KBr + HBr + CO + CO_2.}$$

This is a net balance, not a claim about every elementary step.

The final acid–base interconversion is therefore

$$\mathrm{[P(L)(OH)F]^+ + OH^- \rightleftharpoons P(L)(O)F + H_2O.}$$

The neutral product is **fluorido(oxo)(octaethylporphyrinato)phosphorus(V)**. Its charge-separated SMILES is:

`CCC1=C(CC)C2=[N+]3C1=Cc1c(CC)c(CC)c4n1[P-]31([O-])(F)n3c(c(CC)c(CC)c3=CC3=[N+]1C(=C4)C(CC)=C3CC)=C2`

In the requested drawing, represent its axial oxygen as $\mathrm{P{=}O}$.

Finally, different axial groups in **Y3** remove the horizontal mirror plane that would exchange them. The four vertical mirror planes remain in the idealized geometry, explaining the stated loss of exactly one plane.

9.7 — Sandwich structures

The approximate cavity radius is

$$r \approx \frac{4.0}{2} = 2.0\ \text{Å}.$$

All three supplied metal–N distances exceed this radius, so the metals must lie outside the individual N-donor planes in the proposed structures. For an ideal planar, centred N-donor square,

$$h = \sqrt{d_{\mathrm{M-N}}^2 - r^2}.$$

Metal	$d_{\mathrm{M-N}}$	Approximate height h above an N-donor plane
Zr	2.4 Å	1.3 Å
Eu	2.5 Å	1.5 Å
Bi	2.3 Å	1.1 Å

These are geometric estimates using the approximate cavity size.

$\mathrm{Zr(OEP)_2$: bis(octaethylporphyrinato)zirconium(IV).

Draw two parallel, cofacial porphyrin decks with Zr between their centres. Zr binds all four N donors of each deck, giving coordination number eight. A 45° offset between the N-donor squares gives a square-antiprismatic arrangement with four vertical mirror planes.

SMILES:
`CCC1=C(CC)c2cc3c(CC)c(CC)c4cc5[n]6->[Zr+4]789%10(<-[n]2c1cc1c(CC)c(CC)c(cc6C(CC)=C5CC)[n-]->71)(<-[n]1c2cc5c(CC)c(CC)c(cc6[n]->8c(cc7c(CC)c(CC)c(cc1C(CC)=C2CC)[n-]->97)C(CC)=C6CC)[n-]->%105)<-[n-]34`

$\mathrm{Eu_2(OEP)_3$: tris(octaethylporphyrinato)dieuropium(III).

Draw three parallel decks in the sequence

porphyrin–Eu–porphyrin–Eu–porphyrin.

Each Eu binds the four nitrogens of each adjacent deck. The middle porphyrin coordinates both metals, one on each face. An arrangement with aligned outer decks and a middle deck rotated by 45° satisfies the required symmetry.

SMILES:
`CCC1=C(CC)c2cc3c(CC)c(CC)c4cc5[n]6->[Eu+3]789%10(<-[n]2c1cc1c(CC)c(CC)c(cc6C(CC)=C5CC)[n-]->71)(<-[n-]34)<-[n]12->[Eu+3]34567(<-[n]%11c%12cc%13c(CC)c(CC)c(cc%14[n]->3c(cc3c(CC)c(CC)c(cc%11C(CC)=C%12CC)[n-]->43)C(CC)=C%14CC)[n-]->5%13)<-[n]->83c4cc5c(CC)c(CC)c(cc1C(CC)=C(CC)c2cc1c(CC)c(CC)c(cc3C(CC)=C4CC)[n-]->9->61)[n-]->%10->75`

$\mathrm{Bi_2(OEP)_2Cl_2}$**: di-μ-chlorido-bis[(octaethylporphyrinato)bismuth(III)].**

Draw two parallel porphyrins, each binding one Bi displaced toward the space between the decks. Join the two Bi atoms through **two bridging chlorides**, giving a central $\mathrm{Bi_2Cl_2}$ four-membered ring:

$$\mathrm{L Bi(\mu\text{-}Cl)_2 Bi L}.$$

Each Bi has four N donors and two chloride contacts. A symmetric arrangement with eclipsed decks has three mirror planes: the plane of the $\mathrm{Bi_2Cl_2}$ ring, a perpendicular plane through the Bi–Bi axis, and the plane midway between the porphyrin decks. No Bi–Bi bond is required.

SMILES:
`CCC1=C(CC)c2cc3c(CC)c(CC)c4cc5[n]6->[Bi+3]78(<-[Cl-]->[Bi+3]9%10%11(<-[Cl-]->7)<-[n]7c%12cc%13c(CC)c(CC)c(cc%14[n]->9c(cc9c(CC)c(CC)c(cc7C(CC)=C%12CC)[n-]->%109)C(CC)=C%14CC)[n-]->%11%13)(<-[n]2c1cc1c(CC)c(CC)c(cc6C(CC)=C5CC)[n-]->81)<-[n-]34`

The oxidation-state balances are, respectively,

$$+4 + 2(-2) = 0, \qquad 2(+3) + 3(-2) = 0, \qquad 2(+3) + 2(-2) + 2(-1) = 0.$$

The SMILES encode coordination connectivity; they do not encode the deck rotations just described.

9.8 — Bonding orbitals

Take the metal–metal axis as z, pointing right in the printed coordinate system. Use two colours or $+/-$ signs to denote orbital phase. In every bonding combination, **overlapping lobes in the internuclear region must have the same phase**.

Orbital	Precise drawing description	Nodal planes containing the M–M axis
$\sigma(\mathrm{d}_{z^2} + \mathrm{d}_{z^2})$	On each metal, draw two lobes along z and an opposite-phase torus around the metal in the xy plane. The two facing axial lobes have the same phase and overlap end-on.	None
$\pi(\mathrm{d}_{xz} + \mathrm{d}_{xz})$	Draw four lobes on each metal in the xz plane, between the x and z axes. Match phases across the internuclear region both above and below the z axis; the upper and lower overlap regions have opposite phases.	yz
$\pi(\mathrm{d}_{yz} + \mathrm{d}_{yz})$	Draw the analogous four-lobed orbitals in the yz plane. Match phases across the internuclear region on both sides along y.	xz
$\delta(\mathrm{d}_{xy} + \mathrm{d}_{xy})$	Draw four lobes around each metal in its xy plane, between the x and y axes. Corresponding lobes on the two metals overlap face-to-face with matching phases. Adjacent quadrants have opposite phases.	xz and yz

The overall sign of an atomic orbital is arbitrary. For the π combinations, choose the relative atomic-orbital phases so that the "+" combinations printed in the question are constructive.

9.9 — Metal–metal bond orders

Each porphyrinato ligand contributes charge -2. The supplied MO ordering is

$$\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*,$$

where each π level contains two orbitals. Bond order is

$$\mathrm{BO} = \frac{N_{\mathrm{bonding}} - N_{\mathrm{antibonding}}}{2}.$$

Complex	Metal oxidation states	Total d-electrons	Occupancy	Bond order
$[\mathrm{Mo(OEP)}]_2$	Two Mo(II)	$2(6-2) = 8$	$\sigma^2\pi^4\delta^2$	$(8-0)/2 = \boxed{4}$
$[\mathrm{Ir(OEP)}]_2$	Two Ir(II)	$2(9-2) = 14$	$\sigma^2\pi^4\delta^2(\delta^*)^2(\pi^*)^4$	$(8-6)/2 = \boxed{1}$
$[\mathrm{Re(OEP)}]_2^+$	Oxidation-state sum $+5$	$2(7) - 5 = 9$	$\sigma^2\pi^4\delta^2(\delta^*)^1$	$(8-1)/2 = \boxed{3.5}$

For the Re cation, the average oxidation state is $+2.5$; assigning the positive charge to a particular metal is unnecessary.

9.10 — Effect of a 45° rotation

σ/σ^***: b, remains unchanged.**

The d_{z^2} orbital is rotationally symmetric about the metal–metal axis. Rotating a porphyrin around z therefore leaves the σ interaction unchanged.

π/π^***: b, remains unchanged.**

Both members of the degenerate $\{\mathrm{d}_{xz}, \mathrm{d}_{yz}\}$ pair must be considered. Rotation changes their basis according to

$$\begin{pmatrix} \mathrm{d}'_{xz} \\ \mathrm{d}'_{yz} \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \mathrm{d}_{xz} \\ \mathrm{d}_{yz} \end{pmatrix}.$$

This mixes the two orbitals without changing the available π subspace or its bonding–antibonding splitting. Although an individual same-label overlap decreases, cross-overlap with the other π orbital compensates for it.

δ/δ^***: d, decreases to zero.**

For the retained d_{xy}-based interaction, the overlap varies as

$$S_\delta(\theta) \propto \cos(2\theta).$$

Thus, at 45°,

$$S_\delta(45^\circ) \propto \cos 90^\circ = 0.$$

Positive and negative overlap contributions cancel, so the δ and δ^* levels become nonbonding and degenerate in the stated model.

This also explains why 7, 8, or 9 d-electrons favour eclipsing: those occupancies give a net δ-bonding contribution, which is lost on staggering.

The solution was checked against the official solution.