

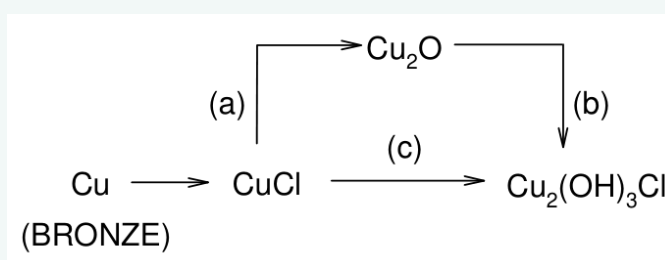
IChO 1995

Theory problems and solutions · Beijing, China · 6 theory problems with complete solutions

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Problem 1: Corrosion of ancient bronze and a Cu-Zn alloy

1.1 Excavated Chinese ancient bronze musical instrument, carillon, was covered entirely by rust. Chemical analysis showed that the rust contains CuCl , Cu_2O and $\text{Cu}_2(\text{OH})_3\text{Cl}$. Simulation experiments showed that CuCl was formed first under the action of both air and Cl containing aqueous solution and then $\text{Cu}_2(\text{OH})_3\text{Cl}$ produced through the following two different ways:



Using the molar standard formation Gibbs free energies of the species concerned answer the following questions:

Species	$\text{Cu}_2\text{O}(\text{s})$	$\text{CuO}(\text{s})$	$\text{CuCl}(\text{s})$	$\text{Cu}_2(\text{OH})_3\text{Cl}(\text{s})$	$\text{Cl}(\text{aq})$	$\text{OH}(\text{aq})$	$\text{H}_2\text{O}(\text{l})$
$\Delta_f G^0(298 \text{ K}) (\text{kJ mol}^{-1})$	-146	-130	-120	-1338	-131	-157	-237

- Write balanced equations for reactions (a), (b) and (c).
- Calculate the molar standard Gibbs free energy $\Delta_f G^0(298 \text{ K})$ for reactions (a), (b) and (c).
- Decide the spontaneous direction of reaction (a) in air through calculation, when $T = 298 \text{ K}$, $c(\text{HCl}) = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$.

1.2 Rate constants k_c for reaction (c) were measured at various temperatures in a simulation experiment in order to obtain its kinetic parameters. On the basis of the data given below answer the following questions:

$t / ^\circ\text{C}$	25	40
$k_c / \text{mol dm}^{-3} \text{ s}^{-1}$	1.29×10^{-4}	2.50×10^{-4}

- Write the equation for calculating the activation energy of reaction (c) and find the value.
- Assign the overall reaction order of reaction (c).
- Knowing that the rate determining step of reaction (c) is the monolayer adsorption of $\text{O}_2(\text{g})$ on solid CuCl , write the overall rate equation of this heterogeneous reaction (c). Under what condition might the reaction order be the same as that you have given in ii)? Assume only O_2 can be adsorbed.

1.3 A copper plate was divided into two parts, $\text{Cu}(1)$ and $\text{Cu}(2)$. $\text{Cu}(1)$ was then hammered so that $\text{Cu}(1)$ and $\text{Cu}(2)$ are different in certain thermodynamic properties.

i) An galvanic cell with Cu(1) and Cu(2) was designed as Cu(1)|CuSO₄(aq)|Cu(2) and the electromotive force E of the above cell was expressed as $E = \Phi_R - \Phi_L$, where Φ_R and Φ_L being the right and left electrode potentials (i. e. half-cell potentials), respectively. Please choose the correct E value from the following and give the thermodynamic reason for your choice.

(A) $E < 0$ (B) $E = 0$ (C) $E > 0$ (D) It cannot be decided

ii) Write the net cell reaction for the cell.

1.4 In a Cu–Zn alloy the molar fractions of Cu and Zn are 0.750 and 0.250, respectively. The structure type of the alloy is the same as that of pure copper, except Zn atoms substitute some Cu atoms randomly and statistically, i. e. at every atomic position, the probability of the occupation of Cu and Zn is proportional to the composition of the alloy. In this sense the alloy can be considered as composed of statistical atoms Cu_{*x*}Zn_{1–*x*}. X-ray analysis shows that the arrangement of atoms in the alloy is of the cubic face-centred close packing type. Density of the alloy $d = 8.51 \text{ g cm}^{-3}$. Calculate the radius of the statistical atoms in the alloy.

Given: $A_r(\text{Cu}) = 63.5$, $A_r(\text{Zn}) = 65.4$.

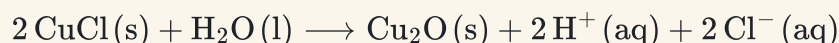
Official English text of the problem.

Answers

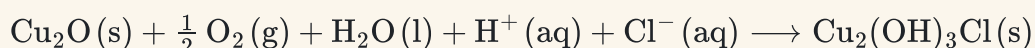
The reaction Gibbs energies below refer to the equations **as written**, each involving two copper atoms.

- **1.1(i)**

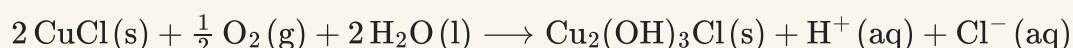
(a)



(b)



(c)



- **1.1(ii)**

$$\Delta_r G_a^\circ = +69, \quad \Delta_r G_b^\circ = -824, \quad \Delta_r G_c^\circ = -755 \text{ kJ mol}^{-1}$$

- **1.1(iii)** $\Delta_r G_a = -22.3 \text{ kJ mol}^{-1}$. Reaction (a) proceeds spontaneously **toward** Cu₂O.

- **1.2(i)**

$$E_a = \frac{R \ln(k_{c,2}/k_{c,1})}{1/T_1 - 1/T_2} = \boxed{34.2 \text{ kJ mol}^{-1}}.$$

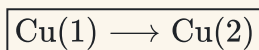
- **1.2(ii)** The measured overall reaction order is $\boxed{0}$.

- **1.2(iii)** The intended Langmuir saturation rate law is

$$v = k_{\text{sat}} \frac{K_{\text{ads}} p_{\text{O}_2}}{1 + K_{\text{ads}} p_{\text{O}_2}}.$$

It becomes zero order when $K_{\text{ads}} p_{\text{O}_2} \gg 1$, with $k_c = k_{\text{sat}}$.

- **1.3(i)** $(C) E > 0$, because hammered copper has the higher chemical potential.
- **1.3(ii)**



Copper dissolves from the hammered electrode and deposits on the unhammered electrode.

- **1.4**

$$r = 1.30 \times 10^{-8} \text{ cm} = 130 \text{ pm}.$$

Solution

Chemical names and SMILES

These names and representations apply throughout the solution.

Species	Name	SMILES
H ₂ O	Water	O
O ₂	Dioxygen	O=O
H ⁺	Hydrogen ion, using the thermodynamic proton convention	[H+]
Cl ⁻	Chloride ion	[Cl-]
OH ⁻	Hydroxide ion	[OH-]
Cu ²⁺	Copper(II) ion	[Cu+2]
SO ₄ ²⁻	Sulfate ion	[O-]S(=O)(=O)[O-]
HCl(aq)	Hydrochloric acid, represented as dissociated ions	[H+] . [Cl-]
CuCl	Copper(I) chloride	[Cu+] . [Cl-]
Cu ₂ O	Copper(I) oxide	[Cu+] . [Cu+] . [O-2]
CuO	Copper(II) oxide	[Cu+2] . [O-2]
Cu ₂ (OH) ₃ Cl	Copper(II) hydroxychloride, or basic copper(II) chloride	[Cu+2] . [Cu+2] . [OH-] . [OH-] . [OH-] . [Cl-]
CuSO ₄	Copper(II) sulfate	[Cu+2] . [O-]S(=O)(=O)[O-]

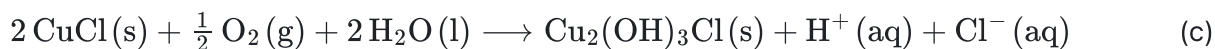
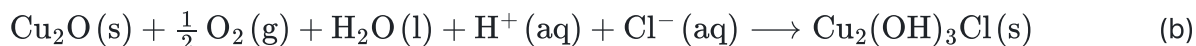
The disconnected SMILES for ionic solids specify composition and formal charges; they do not describe crystal connectivity or coordination geometry. Copper and zinc have atomic representations [Cu] and [Zn], but these do not encode metallic lattices or deformation. A statistical alloy atom is an average lattice-site description and has no molecular SMILES.

1.1(i) Balanced reactions

In reaction (a), copper remains in oxidation state +1: copper(I) chloride hydrolyses to copper(I) oxide.



In $\text{Cu}_2(\text{OH})_3\text{Cl}$, three hydroxide ions and one chloride ion have total charge -4 , so both copper atoms are in oxidation state $+2$. Therefore, reactions (b) and (c) require oxidation of copper(I). Dioxygen supplies the oxidizing agent.



Each equation balances both atoms and charge. Adding (a) and (b), then cancelling common species, gives (c).

1.1(ii) Standard reaction Gibbs energies

For a balanced reaction,

$$\Delta_r G^\circ = \sum_{\text{products}} \nu_i \Delta_f G_i^\circ - \sum_{\text{reactants}} \nu_i \Delta_f G_i^\circ.$$

We use the conventional values

$$\Delta_f G^\circ[\text{H}^+(\text{aq})] = 0, \quad \Delta_f G^\circ[\text{O}_2(\text{g})] = 0,$$

and the supplied value $-1338 \text{ kJ mol}^{-1}$ for $\text{Cu}_2(\text{OH})_3\text{Cl(s)}$.

For (a),

$$\begin{aligned} \Delta_r G_a^\circ &= [-146 + 2(-131)] - [2(-120) + (-237)] \\ &= \boxed{+69 \text{ kJ mol}^{-1}}. \end{aligned}$$

For (b),

$$\begin{aligned} \Delta_r G_b^\circ &= -1338 - [(-146) + (-237) + (-131)] \\ &= \boxed{-824 \text{ kJ mol}^{-1}}. \end{aligned}$$

For (c),

$$\begin{aligned} \Delta_r G_c^\circ &= [-1338 + (-131)] - [2(-120) + 2(-237)] \\ &= \boxed{-755 \text{ kJ mol}^{-1}}. \end{aligned}$$

The independent calculations satisfy Hess's law:

$$69 - 824 = -755 \text{ kJ mol}^{-1}.$$

If equations (b) and (c) are doubled to give integer coefficients, their reaction Gibbs energies also double, to -1648 and $-1510 \text{ kJ mol}^{-1}$, respectively.

1.1(iii) Spontaneous direction at the specified acid concentration

For reaction (a), the activities of the pure solids and liquid water are taken as unity. Therefore,

$$Q_a = a_{\text{H}^+}^2 a_{\text{Cl}^-}^2.$$

Treating the dilute hydrochloric acid as fully dissociated and approximating activities by concentrations divided by $c^\circ = 1 \text{ mol dm}^{-3}$,

$$a_{\text{H}^+} \simeq a_{\text{Cl}^-} \simeq 1.0 \times 10^{-4},$$

so

$$Q_a = (10^{-4})^2 (10^{-4})^2 = 10^{-16}.$$

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

$$\begin{aligned}\Delta_r G_a &= \Delta_r G_a^\circ + RT \ln Q_a \\ &= 69.0 + \frac{(8.314)(298) \ln(10^{-16})}{1000} \\ &= 69.0 - 91.3 \\ &= \boxed{-22.3 \text{ kJ mol}^{-1}}.\end{aligned}$$

Thus, under the specified conditions, reaction (a) proceeds spontaneously to the right, producing copper(I) oxide. Oxygen pressure does not enter this calculation because reaction (a) itself does not consume oxygen.

1.2(i) Activation energy

The Arrhenius equation is

$$k_c = Ae^{-E_a/(RT)}.$$

Taking the ratio at two temperatures eliminates A :

$$\ln \left(\frac{k_{c,2}}{k_{c,1}} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

With $T_1 = 298.15 \text{ K}$ and $T_2 = 313.15 \text{ K}$,

$$\begin{aligned}E_a &= \frac{(8.314) \ln [(2.50 \times 10^{-4})/(1.29 \times 10^{-4})]}{1/298.15 - 1/313.15} \\ &= 3.424 \times 10^4 \text{ J mol}^{-1} \\ &= \boxed{34.2 \text{ kJ mol}^{-1}}.\end{aligned}$$

This is the apparent activation energy associated with the measured rate constant.

1.2(ii) Overall reaction order

For an overall order n , a concentration-based rate constant has dimensions

$$[k] = (\text{mol dm}^{-3})^{1-n} \text{s}^{-1}.$$

The supplied units are

$$[k_c] = \text{mol dm}^{-3} \text{s}^{-1}.$$

Hence $1 - n = 1$, giving

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

Thus, under the measurement conditions, $v = k_c$.

1.2(iii) Surface rate equation and zero-order limit

The intended model is single-component Langmuir adsorption on a fixed population of surface sites. Let $p = p_{\text{O}_2}$, and let K_{ads} be an adsorption parameter with reciprocal-pressure units.

For molecular adsorption, the occupied fraction of the surface is

$$\theta = \frac{K_{\text{ads}} p}{1 + K_{\text{ads}} p}.$$

The corresponding phenomenological saturation rate equation is

$$v = k_{\text{sat}} \frac{K_{\text{ads}} p}{1 + K_{\text{ads}} p}.$$

Equivalently, it can be written as $v = k' p / (1 + K_{\text{ads}} p)$, where $k' = k_{\text{sat}} K_{\text{ads}}$. The coefficient k_{sat} includes the available reactive surface per unit reaction volume.

At sufficiently high oxygen pressure or sufficiently strong adsorption,

$$K_{\text{ads}} p \gg 1, \quad \theta \simeq 1,$$

and therefore

$$v \simeq k_{\text{sat}} = k_c.$$

The surface is effectively saturated, and the reaction is zero order in oxygen, agreeing with part (ii). This conclusion assumes that the exposed surface area remains effectively constant.

At low coverage,

$$K_{\text{ads}} p \ll 1, \quad v \simeq k_{\text{sat}} K_{\text{ads}} p,$$

so the same model predicts first-order dependence on oxygen pressure.

1.3(i) Sign of the cell emf

Hammering stores deformation energy in the copper through lattice strain and defects. Consequently, the hammered copper has a greater chemical potential:

$$\mu_1 > \mu_2.$$

Transfer of copper from the hammered to the unhammered state has

$$\Delta_r G = \mu_2 - \mu_1 < 0.$$

The electrode process transfers two electrons per copper atom, so

$$\Delta_r G = -2FE.$$

Thus,

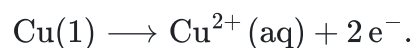
$$E = \frac{\mu_1 - \mu_2}{2F} > 0.$$

The right electrode, unhammered copper, has the higher reduction potential:

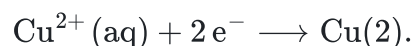
$$\Phi_{\text{R}} > \Phi_{\text{L}}, \quad E > 0, \quad \text{choice (C)}.$$

1.3(ii) Net cell reaction

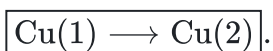
At the left electrode, hammered copper dissolves:



At the right electrode, copper deposits:



Adding these half-reactions gives



The sulfate ion is a spectator.

1.4 Radius of the statistical atoms

The average molar mass per mole of occupied atomic sites is

$$\begin{aligned}\overline{M} &= x_{\text{Cu}}M_{\text{Cu}} + x_{\text{Zn}}M_{\text{Zn}} \\ &= (0.750)(63.5) + (0.250)(65.4) \\ &= 63.975 \text{ g mol}^{-1}.\end{aligned}$$

A face-centred cubic unit cell contains

$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$$

statistical atoms. Its average mass is therefore

$$m_{\text{cell}} = \frac{4\overline{M}}{N_{\text{A}}}.$$

Writing its edge length as a ,

$$d = \frac{m_{\text{cell}}}{a^3} = \frac{4\overline{M}}{N_{\text{A}}a^3}.$$

Using $N_{\text{A}} = 6.022 \times 10^{23} \text{ mol}^{-1}$,

$$\begin{aligned}a &= \left[\frac{4(63.975)}{(8.51)(6.022 \times 10^{23})} \right]^{1/3} \text{ cm} \\ &= 3.682 \times 10^{-8} \text{ cm}.\end{aligned}$$

In the face-centred cubic close-packed model, atoms touch along a face diagonal. That diagonal spans four radii:

$$\sqrt{2}a = 4r.$$

Hence,

$$\begin{aligned}r &= \frac{a}{2\sqrt{2}} \\ &= 1.302 \times 10^{-8} \text{ cm} \\ &= \boxed{130 \text{ pm}}.\end{aligned}$$

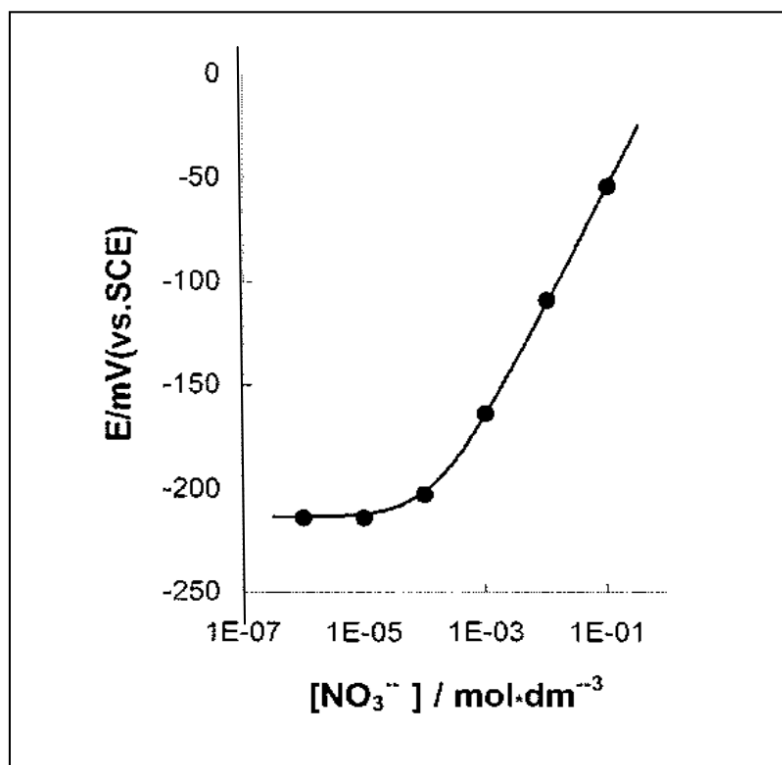
This is the effective radius of the average statistical atom, rather than a separately determined radius for each element.

The solution was checked against the official solution.

Problem 2: Nitrate in milk serum: ion-selective electrode

To control the quality of milk serum, a dairy by-product, the concentration of NO_3^- ion in serum is monitored by means of an ion selective electrode. Generally there is about 15 mg NO_3^- ion per litre in serum, measured on the basis of nitrogen mass.

2.1 For a nitrate ion selective electrode a calibration curve as shown below was obtained using a series of standard nitrate solutions containing $0.5 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$, $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $2.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cl}^-$ ion as the background. Decide whether it is feasible to measure concentration NO_3^- in serum under the above conditions.



2.2 Given are selective coefficients of Cl^- , SO_4^{2-} and ClO_4^- versus NO_3^- as follow

$$K_{\text{NO}_3^-, \text{Cl}^-} = \frac{c_{\text{NO}_3^-}}{c_{\text{Cl}^-}} = 4.9 \times 10^{-2} \quad K_{\text{NO}_3^-, \text{SO}_4^{2-}} = \frac{c_{\text{NO}_3^-}}{c_{\text{SO}_4^{2-}}^{1/2}} = 4.1 \times 10^{-3}$$

$$K_{\text{NO}_3^-, \text{ClO}_4^-} = \frac{c_{\text{NO}_3^-}}{c_{\text{ClO}_4^-}} = 1.0 \times 10^{-3}$$

where the units of the concentrations are in mol dm^{-3} which is the best to reduce the interference of Cl^- to NO_3^- determination, so as to control the error in the NO_3^- concentration within 1 %, when there are $1.40 \times 10^{-3} \text{ mol dm}^{-3} \text{ NO}_3^-$ and $1.60 \times 10^{-2} \text{ mol dm}^{-3} \text{ Cl}^-$ in serum:



Calculate the amount of the salt that should be added to 1 dm^3 of the sample solution to be measured.

2.3 The NO_3^- ion concentration was determined by this method at 298 K. For 25.00 cm^3 sample solution the electronic potential, E , is measured to be -160 mV . After adding 1.00 cm^3 $1.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ NO}_3^-$ standard solution to the above solution, E changes to -130 mV . Find the pNO_3 of the serum.

2.4 The selective coefficient of CH_3COO^- versus NO_3^- , $K(\text{NO}_3^-/\text{CH}_3\text{COO}^-) = 2.7 \times 10^{-3}$. If AgCH_3COO instead of Ag_2SO_4 is added to the sample solution of question 2.2, find the upper limit of the pH value below which the same requirement in question 2.2 can be met.

$$\begin{aligned} K_{\text{sp}}(\text{AgCl}) &= 3.2 \times 10^{-10} & K_{\text{sp}}(\text{Ag}_2\text{SO}_4) &= 8.0 \times 10^{-5} \\ K_{\text{sp}}(\text{AgCH}_3\text{COO}) &= 8.0 \times 10^{-3} & K_{\text{a}}(\text{CH}_3\text{COOH}) &= 2.2 \times 10^{-5} \\ A_{\text{r}}(\text{N}) &= 14.00 \end{aligned}$$

Official English text of the problem.

Answers

- **2.1: Yes.** The expected nitrate concentration is $1.07 \times 10^{-3} \text{ mol dm}^{-3}$, near the beginning of the approximately linear part of the calibration curve.
- **2.2:** Choose **silver sulfate**, Ag_2SO_4 , SMILES $[\text{Ag}+] \cdot [\text{Ag}+] \cdot [\text{O}-]\text{S}(=\text{O})(=\text{O})[\text{O}-]$. The minimum addition to 1 dm^3 is $7.86 \times 10^{-3} \text{ mol}$, approximately 2.45 g.
- **2.3:** $\text{pNO}_3 = 4.77$, corresponding to $c_{\text{NO}_3^-} = 1.71 \times 10^{-5} \text{ mol dm}^{-3}$.
- **2.4:** The usual quantitative-precipitation approximation gives $\text{pH}_{\text{max}} \approx 4.34$. Retaining both residual chloride and acetate interference gives the slightly stricter limit $\text{pH}_{\text{max}} \approx 4.33$.

Solution

2.1 — Feasibility of the measurement

Nitrate, NO_3^- , has SMILES $[\text{O}-][\text{N}+](=\text{O})[\text{O}-]$. Each nitrate ion contains one nitrogen atom. Because the stated concentration is expressed **as nitrogen mass**,

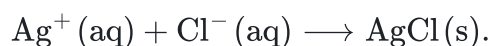
$$c_{\text{NO}_3^-} = \frac{15 \times 10^{-3} \text{ g dm}^{-3}}{14.00 \text{ g mol}^{-1}} = 1.07 \times 10^{-3} \text{ mol dm}^{-3}.$$

The graph becomes approximately linear in E versus $\log c_{\text{NO}_3^-}$ around $10^{-3} \text{ mol dm}^{-3}$, and remains so at higher concentrations. The expected serum concentration therefore lies in the useful, concentration-sensitive region.

Thus, **measurement is feasible using the supplied calibration.**

2.2 — Choice and minimum amount of silver salt

Silver(I) ion, $[\text{Ag}+]$, precipitates chloride, $[\text{Cl}-]$, as silver chloride, $[\text{Ag}+] \cdot [\text{Cl}-]$:



The candidate salts are:

Salt	Name and SMILES	Assessment
AgNO_3	Silver nitrate, $[\text{Ag}+] \cdot [\text{O}-][\text{N}+](=\text{O})[\text{O}-]$	Adds the analyte itself in a large amount.
Ag_2SO_4	Silver sulfate, $[\text{Ag}+] \cdot [\text{Ag}+] \cdot [\text{O}-]\text{S}(=\text{O})(=\text{O})[\text{O}-]$	Suitable because sulfate is already the large, calibrated background.
AgClO_4	Silver perchlorate, $[\text{Ag}+] \cdot [\text{O}-]\text{Cl}(=\text{O})(=\text{O})=\text{O}$	Introduces too much additional perchlorate interference.

Here sulfate is $[\text{O}-]\text{S}(=\text{O})(=\text{O})[\text{O}-]$, and perchlorate is $[\text{O}-]\text{Cl}(=\text{O})(=\text{O})=\text{O}$. These oxyanion SMILES represent individual resonance forms. The disconnected SMILES for salts specify ionic composition; they do not describe crystal lattices.

For silver perchlorate, nearly complete removal of the initial chloride would introduce approximately $0.0160 \text{ mol dm}^{-3}$ perchlorate. Its nitrate-equivalent contribution alone would be

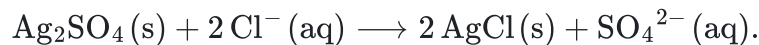
$$(1.0 \times 10^{-3})(1.60 \times 10^{-2}) = 1.60 \times 10^{-5} \text{ mol dm}^{-3},$$

which exceeds the permitted error,

$$B = 0.01(1.40 \times 10^{-3}) = 1.40 \times 10^{-5} \text{ mol dm}^{-3}.$$

Leaving more chloride cannot solve this problem, because chloride has the larger selectivity coefficient.

For **silver sulfate**, the sulfate response is treated as part of the existing 0.5 mol dm^{-3} background, since the solution already contains 0.5 M potassium sulfate. The precipitation reaction is



The maximum permissible residual chloride concentration satisfies

$$K_{\text{NO}_3^-, \text{Cl}^-} c_{\text{Cl}^-} \leq B.$$

Consequently,

$$c_{\text{Cl}^-, \text{max}} = \frac{1.40 \times 10^{-5}}{4.9 \times 10^{-2}} = 2.857 \times 10^{-4} \text{ mol dm}^{-3}.$$

At this boundary, the dissolved silver concentration is

$$c_{\text{Ag}^+} = \frac{K_{\text{sp}}(\text{AgCl})}{c_{\text{Cl}^-}} = \frac{3.2 \times 10^{-10}}{2.857 \times 10^{-4}} = 1.12 \times 10^{-6} \text{ mol dm}^{-3}.$$

The silver added must supply both the precipitated silver chloride and this small dissolved remainder.

Neglecting the volume change on adding solid salt,

$$2n_{\text{Ag}_2\text{SO}_4} = V(c_{\text{Cl}^-,0} - c_{\text{Cl}^-, \text{max}} + c_{\text{Ag}^+}).$$

For $V = 1 \text{ dm}^3$,

$$n_{\text{Ag}_2\text{SO}_4, \text{min}} = \frac{1}{2} (1.60 \times 10^{-2} - 2.857 \times 10^{-4} + 1.12 \times 10^{-6}) = 7.8577 \times 10^{-3} \text{ mol}.$$

Therefore,

$$\boxed{n_{\text{Ag}_2\text{SO}_4, \text{min}} = 7.86 \times 10^{-3} \text{ mol}}.$$

Using $M(\text{Ag}_2\text{SO}_4) \approx 311.8 \text{ g mol}^{-1}$, this is approximately 2.45 g.

The dose is compatible with complete dissolution of the added silver sulfate: at the calculated endpoint,

$$c_{\text{Ag}^+}^2 c_{\text{SO}_4^{2-}} \approx (1.12 \times 10^{-6})^2 (0.51) \approx 6.4 \times 10^{-13} \ll 8.0 \times 10^{-5}.$$

Thus, saturation with solid silver sulfate does not determine the minimum dose.

2.3 — Standard addition

For a monovalent ion at 298 K, the magnitude of the Nernst slope is

$$S = \frac{2.303RT}{F} = 0.05913 \text{ V}.$$

Using the measured-potential polarity shown in the problem, increasing nitrate concentration increases E . Hence

$$E_2 - E_1 = S \log_{10} \frac{c_2}{c_1}.$$

Since $\Delta E = 30 \text{ mV}$,

$$r = \frac{c_2}{c_1} = 10^{30/59.13} = 3.216.$$

Let c be the original nitrate concentration. Including dilution by the added standard,

$$c_2 = \frac{cV_0 + c_s V_s}{V_0 + V_s}.$$

Therefore,

$$c = \frac{c_s V_s}{r(V_0 + V_s) - V_0}.$$

Substitution gives

$$c = \frac{(1.00 \times 10^{-3} \text{ mol dm}^{-3})(0.00100 \text{ dm}^3)}{3.216(0.02600 \text{ dm}^3) - 0.02500 \text{ dm}^3} = 1.706 \times 10^{-5} \text{ mol dm}^{-3}.$$

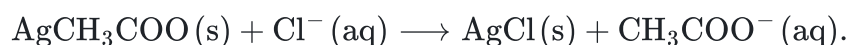
Thus,

$$\text{pNO}_3 = -\log_{10} \left(\frac{c_{\text{NO}_3^-}}{1 \text{ mol dm}^{-3}} \right) = 4.77.$$

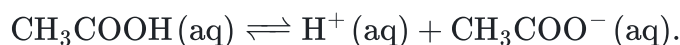
2.4 — Suppressing acetate interference by protonation

The relevant species are silver acetate, AgCH_3COO , $[\text{Ag}^+]$, $\text{CC}(=\text{O})[\text{O}^-]$; acetate, CH_3COO^- , $\text{CC}(=\text{O})[\text{O}^-]$; acetic acid, CH_3COOH , $\text{CC}(=\text{O})\text{O}$; and hydrogen ion, H^+ , $[\text{H}^+]$.

Silver acetate removes chloride through



Acidification suppresses the concentration of interfering acetate:



The combined reaction can be written as



Usual quantitative-precipitation approximation. Removing approximately $0.0160 \text{ mol dm}^{-3}$ chloride introduces the same total concentration of acetate species:

$$C_{\text{Ac}} = c_{\text{CH}_3\text{COO}^-} + c_{\text{CH}_3\text{COOH}} \approx 1.60 \times 10^{-2} \text{ mol dm}^{-3}.$$

If residual chloride interference is neglected, the maximum free acetate concentration is

$$c_{\text{CH}_3\text{COO}^-, \text{max}} = \frac{B}{K_{\text{NO}_3^-, \text{CH}_3\text{COO}^-}} = \frac{1.40 \times 10^{-5}}{2.7 \times 10^{-3}} = 5.185 \times 10^{-3} \text{ mol dm}^{-3}.$$

Using

$$K_a = \frac{c_{\text{H}^+} c_{\text{CH}_3\text{COO}^-}}{c_{\text{CH}_3\text{COOH}}},$$

the minimum hydrogen-ion concentration is

$$\begin{aligned} c_{\text{H}^+, \text{min}} &= K_a \frac{C_{\text{Ac}} - c_{\text{CH}_3\text{COO}^-, \text{max}}}{c_{\text{CH}_3\text{COO}^-, \text{max}}} \\ &= (2.2 \times 10^{-5}) \frac{0.0160 - 0.005185}{0.005185} = 4.589 \times 10^{-5} \text{ mol dm}^{-3}. \end{aligned}$$

Therefore,

$$\text{pH}_{\text{max}} \approx 4.34.$$

Lower pH increases protonation and reduces acetate interference.

Retaining both interferences. The chloride concentration allowed at the minimum sulfate dose in 2.2 already consumes the entire 1% error allowance. With acetate present, chloride must be precipitated more completely.

To find the strict maximum pH, let $x = c_{\text{Cl}^-}$, and let

$$\alpha = \frac{K_a}{K_a + c_{\text{H}^+}}$$

be the fraction of total acetate present as acetate ion. Silver chloride equilibrium and the silver balance give

$$c_{\text{Ag}^+} = \frac{K_{\text{sp}}(\text{AgCl})}{x},$$

$$C_{\text{Ac}} = 0.0160 - x + \frac{K_{\text{sp}}(\text{AgCl})}{x}.$$

The combined nitrate-equivalent interference is consequently

$$\Delta c = k_{\text{Cl}}x + k_{\text{Ac}}\alpha \left(0.0160 - x + \frac{K_{\text{sp}}}{x} \right),$$

where $k_{\text{Cl}} = 0.049$ and $k_{\text{Ac}} = 0.0027$.

Writing $b = k_{\text{Ac}}\alpha$,

$$\Delta c = 0.0160b + (k_{\text{Cl}} - b)x + \frac{bK_{\text{sp}}}{x}.$$

For a fixed pH, its minimum over the silver acetate dose is

$$\Delta c_{\text{min}} = 0.0160b + 2\sqrt{(k_{\text{Cl}} - b)bK_{\text{sp}}}.$$

Setting this equal to $B = 1.40 \times 10^{-5}$ gives

$$\alpha = 0.31874, \quad c_{\text{H}^+} = K_a \frac{1 - \alpha}{\alpha} = 4.702 \times 10^{-5} \text{ mol dm}^{-3},$$

and therefore

$$\boxed{\text{pH}_{\text{max}} = 4.3277 \approx 4.33}.$$

This boundary is attainable with approximately

$$c_{\text{Cl}^-} = 2.39 \times 10^{-6} \text{ mol dm}^{-3}, \quad C_{\text{Ac}} = 0.01613 \text{ mol dm}^{-3},$$

corresponding to 0.01613 mol silver acetate per litre. Its dissolved-ion product is only

$$c_{\text{Ag}^+}c_{\text{CH}_3\text{COO}^-} \approx 6.9 \times 10^{-7} < K_{\text{sp}}(\text{AgCH}_3\text{COO}),$$

so silver acetate solubility does not prevent this result.

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

Problem 3: Glyceraldehyde and its cyclic dimer

1,3-Dihydroxyacetone can be converted to glyceraldehyde. On standing this glyceraldehyde changes spontaneously into a six member cyclic dimer $C_6H_{12}O_6$. The infrared spectrum of the dimer shows no absorption peak between $1600 - 1800\text{ cm}^{-1}$ and the dipole moment of the dimer is determined to be zero.

3.1 Write the Fischer projection structural formula(e) for the resulting glyceraldehyde and indicate configuration using D(+) and/or L(-).

3.2 Write the structural formula for the reaction intermediate of the conversion of 1,3-dihydroxyacetone to glyceraldehyde.

3.3 Write the structural formula for the dimer.

3.4 Using Haworth projection formula represent the possible stereoisomers which fit the dipole moment data.

3.5 Denote each chiral carbon atom in the above formulae with *R* or *S*.

Official English text of the problem.

Answers

- 3.1:** A racemic mixture of **D(+)-glyceraldehyde**, (2R)-2,3-dihydroxypropanal, $O=C[C@H](O)CO$, and **L(-)-glyceraldehyde**, (2S)-2,3-dihydroxypropanal, $O=C[C@@H](O)CO$. In their Fischer projections, place CHO above and CH_2OH below; OH is on the right for D(+) and on the left for L(-).
- 3.2:** The **1,2-enediol**, prop-1-ene-1,2,3-triol, $HO-CH=C(OH)-CH_2OH$, $OC=C(O)CO$.
- 3.3:** The cyclic bis-hemiacetal **3,6-bis(hydroxymethyl)-1,4-dioxane-2,5-diol**, $O1C(O)C(CO)OC(O)C1CO$. Its ring sequence is O1-C2-C3-O4-C5-C6; C2 and C5 bear OH, while C3 and C6 bear CH_2OH .
- 3.4:** Two centrosymmetric, meso stereoisomers satisfy the dipole-moment condition:

I: (2R,3R,5S,6S)-3,6-bis(hydroxymethyl)-1,4-dioxane-2,5-diol, $O1[C@@H](O)[C@@H](CO)O[C@H](O)[C@@H]1CO$. Each adjacent hydroxyl/hydroxymethyl pair is **cis**.

II: (2S,3R,5R,6S)-3,6-bis(hydroxymethyl)-1,4-dioxane-2,5-diol, $O1[C@H](O)[C@@H](CO)O[C@@H](O)[C@@H]1CO$. Each adjacent hydroxyl/hydroxymethyl pair is **trans**.

- 3.5:** D(+)-glyceraldehyde is *R*; L(-)-glyceraldehyde is *S*. For ring positions **C2, C3, C5, C6**, respectively, dimer **I** is *R, R, S, S*, and dimer **II** is *S, R, R, S*. The enediol has no chiral carbon atoms.

Solution

3.1 — Glyceraldehyde formation and Fischer projections

The starting compound, **1,3-dihydroxyacetone** (1,3-dihydroxypropan-2-one), $\text{OCC}(=\text{O})\text{CO}$, is achiral. Conversion of its ketone group into a terminal aldehyde creates a stereogenic centre at C2. With no chiral reagent or catalyst specified, the two enantiomers form in equal amounts.

Draw the Fischer projections with the carbon chain vertical:

Position	D(+)-glyceraldehyde	L(-)-glyceraldehyde
Top	CHO	CHO
Left of central carbon	H	OH
Right of central carbon	OH	H
Bottom	CH ₂ OH	CH ₂ OH

As usual for Fischer projections, horizontal bonds point toward the viewer and vertical bonds point away. The mixture is racemic and therefore has zero net optical rotation.

3.2 — The reaction intermediate

The ketose–aldose conversion proceeds through the enediol:



Each species has molecular formula $\text{C}_3\text{H}_6\text{O}_3$, so both steps are balanced tautomerizations.

In the first step, proton transfers and redistribution of the carbonyl π electrons generate the C1–C2 double bond and the second hydroxyl group. In the second step, the terminal hydroxyl oxygen forms the aldehyde carbonyl while C2 receives a proton.

C2 is planar in the enediol. Protonation from its two faces produces the two glyceraldehyde configurations equally. The intermediate's E/Z geometry need not be specified for this conclusion.

3.3 — Connectivity of the cyclic dimer

The missing carbonyl absorption indicates that the aldehyde groups have been consumed. Each glyceraldehyde molecule supplies:

- Its aldehyde carbon as a hemiacetal carbon.
- Its C2 hydroxyl oxygen as an ether oxygen in the ring.

The C2 hydroxyl oxygen of one molecule attacks the aldehyde carbon of the other; the carbonyl π electrons move onto oxygen, and proton transfer gives a hemiacetal. The corresponding reaction between the remaining hydroxyl and aldehyde groups closes the ring.

Each molecule contributes two carbons and one oxygen to the ring, giving six ring atoms. The connectivity, with the final carbon bonded back to the initial oxygen, is



Thus the product is the **cyclic bis-hemiacetal** identified in Answer 3.3. Its two former carbonyl oxygens are now hydroxyl oxygens.

The balanced dimerization is



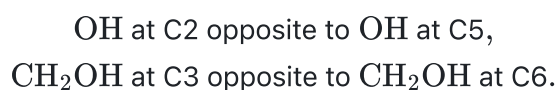
No water is eliminated. Formation of the two hemiacetal linkages preserves all atoms of the two monomers.

3.4 — Haworth projections and the zero dipole moment

Use the following precise Haworth convention:

- Viewed from above the ring, the atoms run **clockwise** as O1–C2–C3–O4–C5–C6.
- Draw O1 at the upper right, C2 at the right, C3 at the lower right, O4 at the lower left, C5 at the left, and C6 at the upper left.
- “Up” and “down” mean above and below the ring plane. At each substituted carbon, its hydrogen points to the opposite face.

An inversion centre at the ring centre exchanges **O1 with O4, C2 with C5, and C3 with C6**. Therefore, corresponding substituents must occupy opposite faces:



The two distinct Haworth projections are:

Dimer	C2–OH	C3–CH ₂ OH	C5–OH	C6–CH ₂ OH
I	Up	Up	Down	Down
II	Down	Up	Up	Down

In **I**, each adjacent hydroxyl/hydroxymethyl pair lies on the same face; in **II**, each pair lies on opposite faces. Reversing all four up/down entries does not give additional stereoisomers: the resulting configurations are equivalent after exchanging the two identical halves.

These configurations permit centrosymmetric chair conformations, with corresponding side chains also related by inversion. Since inversion reverses a dipole vector while leaving such a molecule unchanged,

$$\mu = -\mu \implies \mu = 0.$$

Both structures are meso and contain one D-glyceraldehyde residue and one L-glyceraldehyde residue. Haworth projections and stereochemical SMILES specify their configurations; they do not imply that the actual ring is flat.

3.5 — Absolute configurations

For glyceraldehyde, the priorities at C2 are



The aldehyde carbon outranks the hydroxymethyl carbon because the carbonyl double bond is treated as attachment to two oxygens in the CIP comparison. Applying these priorities to the Fischer projections gives **D(+): R** and **L(-): S**.

For the dimer:

- **At C2 and C5:** ring oxygen > hydroxyl oxygen > neighbouring ring carbon > hydrogen. The ring oxygen outranks the hydroxyl oxygen because it is attached to carbon rather than hydrogen.
- **At C3 and C6:** ring oxygen > neighbouring hemiacetal carbon > hydroxymethyl carbon > hydrogen. The hemiacetal carbon has two oxygen neighbours, whereas the hydroxymethyl carbon has only one.

With the clockwise Haworth convention defined above, an up hydroxyl at C2/C5 gives *R*, and an up hydroxymethyl group at C3/C6 also gives *R*. Down gives *S*.

Structure	C2	C3	C5	C6
Dimer I	<i>R</i>	<i>R</i>	<i>S</i>	<i>S</i>
Dimer II	<i>S</i>	<i>R</i>	<i>R</i>	<i>S</i>

The original glyceraldehyde stereocentres become C3 and C6 without changing configuration. The two additional stereocentres, C2 and C5, arise during hemiacetal formation.

The solution was checked against the official solution.

Problem 4: Bacterial poly(3-hydroxyalkanoic acids)

Poly[(R)-3-hydroxyalkanoic acids], PHAs, are synthesized by a variety of bacteria and function as intracellular carbon and energy storage materials. These polymers are also biodegradable in environments, such as soil, anaerobic sewage and sea water. The inherent biologically mediated environmental degradability, useful physical properties, slow hydrolytic degradation and other favourable properties make bacterial polyesters exciting materials for both disposable biodegradable plastics (good for a clean environment) and special medical products.

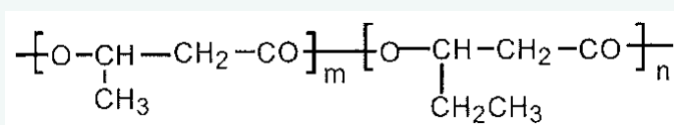
4.1 PHB, Poly(3-hydroxybutanoic acid), produced by bacteria contains only (R)-HB repeating units, while that synthesized by polymer chemists may contain only (R)-HB or only (S)-HB or both (R)- and (S)-HB in an alternating manner or both but in random distributions. Sketch chain structures of the atactic PHB, syndiotactic PHB and isotactic PHBs and denote each chiral carbon with (R) or (S). Five monomeric units are enough for each chain.

{Note: In "PHB", P means "poly" or "polymer of", HB represents the monomeric units contained in poly(3-hydroxybutanoic acid) molecules.}

4.2 Suggest two types of monomers that could be used for polymer chemists to synthesize a PHB, regardless of the stereochemistry of the products.

4.3 Poly[(R)-3-hydroxybutanoic acid] can be synthesized by feeding the bacteria (such as *Alcaligenes Eutrophus*) with sodium acetate in a nitrogen-free media. It is believed that the key steps for the conversion of acetate to PHB are the activation of acetate molecules by coenzyme A and the subsequent formation of the coenzyme A activated acetoacetate, which is then reduced by a reductase to form coenzyme A activated monomer 3-hydroxybutyrate. Polymerization of the monomer is achieved by a polymerase which would build the polymer molecules with unique stereospecificity. Sketch these steps with structural formulae. For coenzyme A the conventional abbreviation, -S-CoA (-CoA is as good), should be used in the sketch.

4.4 If sodium propanoate is used (as the sole carbon source) in the feeding media instead of sodium acetate, the principal product will be a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid with the following generalized structure:



Rationalize the result.

(Note: Two different monomers are needed for the formation of the copolymer. The letters m and n in the structural formula are numbers of the units and have nothing to do with the answer, in other words, you may leave them out in your answer.)

Official English text of the problem.

Answers

In the abbreviated CoA SMILES below, * represents the unchanged CoA residue beyond sulfur, consistent with the abbreviation requested in the problem.

- **4.1:** Along the PHB backbone, representative five-unit configurations are:
- **Atactic:** *R, R, S, S, R*, illustrating an irregular sequence.
- **Syndiotactic:** *R, S, R, S, R*.
- **Isotactic:** *R, R, R, R, R* or *S, S, S, S, S*.

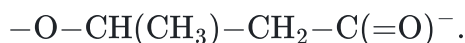
Explicit five-unit structures are given below.

- **4.2:** **3-Hydroxybutanoic acid**, CC(O)CC(=O)O, by polycondensation; and **β-butyrolactone (4-methyloxetan-2-one)**, CC1CC(=O)O1, by ring-opening polymerization.
- **4.3:** Activation gives **acetyl-CoA**, CC(=O)S*. Condensation of two molecules gives **acetoacetyl-CoA**, CC(=O)CC(=O)S*; stereoselective reduction gives **(R)-3-hydroxybutanoyl-CoA**, C[C@H](O)CC(=O)S*, which polymerizes to all-(*R*) PHB.
- **4.4:** Propanoate supplies **propionyl-CoA**, CCC(=O)S*, and, through metabolism, acetyl-CoA. Combining two acetyl units gives the four-carbon monomer; combining acetyl and propionyl units gives **(R)-3-hydroxypentanoyl-CoA**, CC[C@H](O)CC(=O)S*. Incorporation of both activated hydroxyacids produces the copolymer.

Solution

4.1 — Tacticity and five-unit structures

The PHB backbone consists of repetitions of

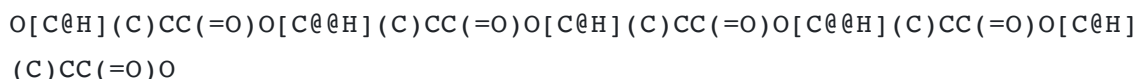


The carbon bearing the methyl group is the stereogenic carbon. Its substituent priorities are oxygen > the chain through CH2C(=O) > methyl > hydrogen.

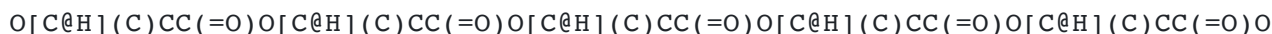
For an explicit sketch, draw five consecutive copies of this backbone and label their stereogenic carbons, from left to right, with the configurations below. The following SMILES represent five-unit chains with hydroxyl and carboxylic acid end groups; these end groups simply make each example a complete molecule.

- **Atactic PHB, illustrative sequence *R, R, S, S, R*:**
O[C@H](C)CC(=O)O[C@H](C)CC(=O)O[C@@H](C)CC(=O)O[C@@H](C)CC(=O)O[C@H](C)CC(=O)O

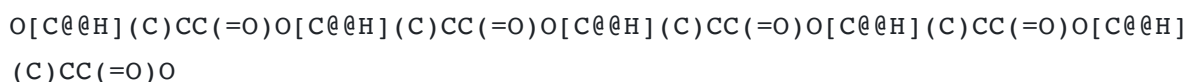
- **Syndiotactic PHB, sequence R, S, R, S, R :**



- **Isotactic poly[(R)-3-hydroxybutanoic acid], sequence R, R, R, R, R :**



- **Isotactic poly[(S)-3-hydroxybutanoic acid], sequence S, S, S, S, S :**

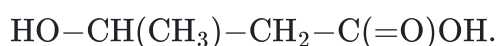


Atactic means that the configurations are distributed randomly along the polymer; the displayed five-unit sequence is one example. Syndiotactic means alternating configurations, whereas isotactic means identical configurations throughout. These descriptions specify configuration independently of the chain's conformation.

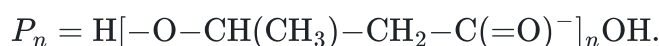
4.2 — Two suitable monomer types

Hydroxyacid route.

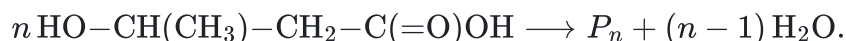
3-Hydroxybutanoic acid, $\text{CC}(\text{O})\text{CC}(=\text{O})\text{O}$, contains both the alcohol and carboxylic acid groups needed for polyester formation:



Define a hydroxyl/carboxyl-ended PHB chain containing n units as



Its polycondensation balance is



There are $n-1$ ester links between n monomers, so $n-1$ molecules of water, O , are eliminated.

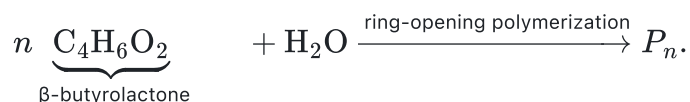
Lactone route.

β -Butyrolactone, or 4-methyloxetan-2-one, $\text{CC1CC}(=\text{O})\text{O1}$, is the corresponding cyclic ester. Its four-membered ring follows the order



with a closing bond from the last carbon back to oxygen. Opening this ring supplies exactly the PHB backbone connectivity.

For the same hydroxyl/carboxyl end groups, the overall balance, including end-group work-up, is



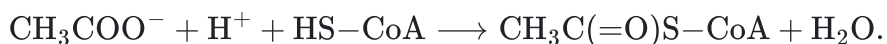
The water accounts for the chosen terminal groups. The stereochemistry of either monomer is unrestricted in this part.

4.3 — Biosynthesis from acetate

Sodium acetate, $\text{CC}(=\text{O})[\text{O}^-] \cdot [\text{Na}^+]$, supplies acetate ion, $\text{CC}(=\text{O})[\text{O}^-]$; sodium ion, $[\text{Na}^+]$, is a spectator.

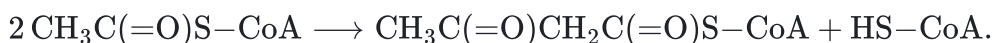
Coenzyme A in its thiol form is written $\text{HS}-\text{CoA}$, with abbreviated SMILES s^* . Below, activation is expressed as its balanced condensation component, driven by metabolic energy coupling. Reduction is expressed as a balanced half-reaction: protons, $[\text{H}^+]$, and electrons represent the reducing equivalents supplied by cellular cofactors.

Activation to acetyl-CoA



The product is **acetyl-CoA**, $\text{CC}(=\text{O})\text{s}^*$, a thioester that activates the acetate-derived acyl group.

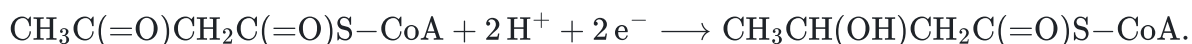
Condensation to acetoacetyl-CoA



The product is **acetoacetyl-CoA (3-oxobutanoyl-CoA)**, $\text{CC}(=\text{O})\text{CC}(=\text{O})\text{s}^*$.

This is a Claisen-type condensation. The carbon nucleophile formed at the methyl group of one acetyl-CoA attacks the thioester carbonyl of another. Acyl substitution forms the carbon-carbon bond and releases coenzyme A. Two two-carbon precursors thereby produce the required four-carbon skeleton.

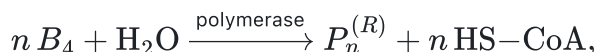
Stereoselective reduction



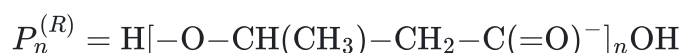
The reductase produces specifically **(R)-3-hydroxybutanoyl-CoA**, $\text{C}[\text{C}@\text{H}](\text{O})\text{CC}(=\text{O})\text{s}^*$, denoted B_4 . Reduction of the ketone creates the stereogenic carbon; the thioester remains available for polymerization.

Polymerization

The hydroxy group and activated carboxyl group of different monomers form ester links, releasing coenzyme A. For the hydroxyl/carboxyl-ended chain used above, the overall balance including hydrolytic termination is



where

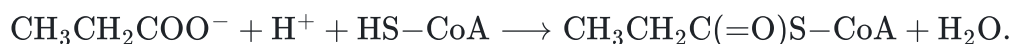


has configuration (R) at every stereogenic carbon.

The water accounts for hydrolysis of the final activated chain end. Ester formation occurs at the acyl carbon, so the (R) configurations of the incorporated monomers are retained.

4.4 — Why propanoate gives both four- and five-carbon repeats

Sodium propanoate, $\text{CCC}(=\text{O})[\text{O}^-] \cdot [\text{Na}^+]$, supplies propanoate ion, $\text{CCC}(=\text{O})[\text{O}^-]$. Its activation gives **propionyl-CoA**, $\text{CCC}(=\text{O})\text{s}^*$:



The carbon source is metabolized before polymer incorporation. Part of the propanoate-derived material supplies acetyl-CoA through oxidative metabolism. A balanced net oxidation expressing this carbon shortening is



Here carbon dioxide is $\text{O}=\text{C}=\text{O}$. This equation gives the overall carbon and redox balance of a multistep conversion.

Consequently, the cells have both two-carbon acetyl-CoA and three-carbon propionyl-CoA available:

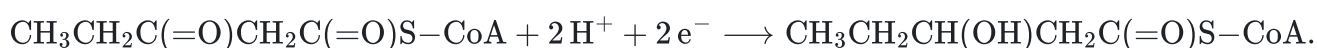
$$\begin{array}{ll} 2 + 2 = 4 & \text{carbons for the HB precursor,} \\ 2 + 3 = 5 & \text{carbons for the HV precursor.} \end{array}$$

The four-carbon route is the acetyl-CoA self-condensation and reduction already shown in 4.3.

For the five-carbon route, acetyl-CoA supplies the carbon nucleophile and propionyl-CoA supplies the acyl group:



The product is **3-oxopentanoyl-CoA**, $\text{CCC}(=\text{O})\text{CC}(=\text{O})\text{S}^*$. Stereoselective reduction then gives



The product is **(R)-3-hydroxypentanoyl-CoA**, $\text{CC}[\text{C}@\text{H}](\text{O})\text{CC}(=\text{O})\text{S}^*$, denoted B_5 .

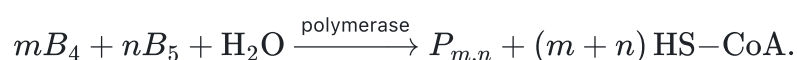
The two activated monomers correspond to:

Hydroxyacid	SMILES	Resulting polyester repeat
(R)-3-Hydroxybutanoic acid	<chem>C[C@H](O)CC(=O)O</chem>	$-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{C}(=\text{O})^-$
(R)-3-Hydroxypentanoic acid	<chem>CC[C@H](O)CC(=O)O</chem>	$-\text{O}-\text{CH}(\text{CH}_2\text{CH}_3)-\text{CH}_2-\text{C}(=\text{O})^-$

Their incorporation produces **poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate]**, commonly called PHBV. An illustrative HB–HV pair, represented as a hydroxyl/carboxyl-ended dimer, has SMILES:



For a chain containing m HB units and n HV units, the corresponding overall polymerization balance is



Thus, one supplied carbon source can generate two distinct activated monomers through metabolism. The generalized formula identifies the two repeat-unit types; it does not determine their sequence or relative amounts.

The solution was checked against the official solution.

Problem 5: Nitric oxide in biology and iron-sulphur nitrosyl complexes

The action of nitric oxide upon human body is dual. The nitric oxide generated in nerve cells will damage the cells, while the nitric oxide generated in endothelial cells of blood vessels can relax the vessels and control blood pressure.

5.1 Indicate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of NO molecule using one of symbols π , σ , π^* or σ^* , and indicate the electron(s) residing in the corresponding orbital using symbols $\uparrow$ and/or $\downarrow$.

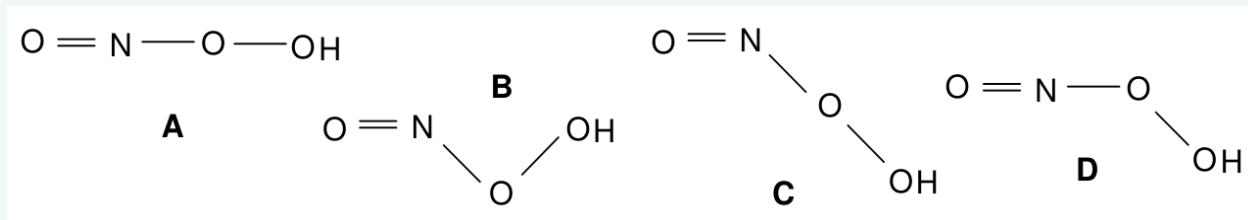
5.2 The relaxation of blood vessels is caused by a series of changes which are mediated by the coordination of NO molecule to iron ion, the latter being a component of an enzyme containing heme. It was known that the coordinated NO behaves as CO molecule (isoelectronic), which one of the following species really exists in the iron complex?

- a) NO b) NO^+ c) NO^-

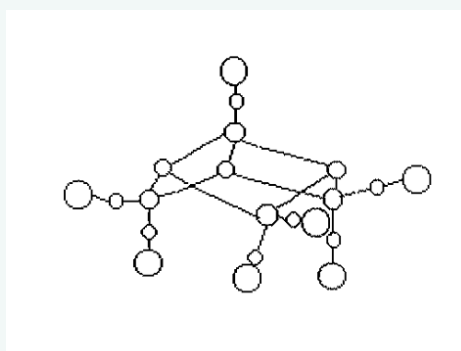
5.3 The cell damage is caused by free radical $\text{OH}\cdot$, which is one of the product of reaction between O_2^- and NO :



in which an intermediate with composition of HOONO is evolved. HOONO is a weak acid. Choose the structural formula with correct bond angles for the intermediate.



5.4 For preservation of meat, sodium nitrite is usually added and as a result NO is, then, formed. Consequently, NO reacts with the sulphur and iron atoms from decomposition of proteins, forming $[\text{Fe}_4\text{S}_3(\text{NO})_7]^-$. The complex anion is bacteriostatic and antiseptic. X-ray crystallography shows that the complex anion has a structure as shown below:



i) Blacken all the circles corresponding to iron atoms and add symbols Fe(A) , Fe(B) , Fe(C) and Fe(D) beside the circles in the sequence of top $\rightarrow$ left $\rightarrow$ right.

ii) The configuration of $3d$ electron shell of the iron atoms has been studied with modern structural analysis. Knowing that the mean oxidation number of the four iron atoms is -0.5 , give their configurations of $3d$ shell, respectively. Assume that each iron atom adopt sp hybridization.

5.5 $[\text{Fe}_4\text{S}_3(\text{NO})_7]^-$ anion can be reduced and a new complex $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$ is formed which contains a cyclic structure unit of Fe_2S_2 .

i) Write the structural formula for the anion $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$.

ii) Give the oxidation state of each iron atom with Arabic numerals.

iii) $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$ can be converted into $[\text{Fe}_2(\text{SCH}_3)_2(\text{NO})_4]^n$, a carcinogen. Which of the following three species is added to $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$: CH_3^+ , $\cdot\text{CH}_3$ or CH_3^- ? Assign the value of n .

Official English text of the problem.

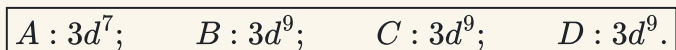
Answers

The complex structures below use extended coordination SMILES: arrows indicate donor-to-metal bonds, and Fe–Fe single bonds represent the localized bonding model explained in the solution. These strings do not specify coordination geometry or spin coupling.

- **5.1:** Nitric oxide, NO, [N]=O: **HOMO** = π^* , **containing** $\uparrow$; **LUMO** = π^* , **empty**, namely the other member of the degenerate pair.
- **5.2: b)** NO^+ , the nitrosonium ion, N#[O+].
- **5.3: B**, peroxyxynitrous acid, HOONO, O=NOO. Both the O=N–O and N–O–O angles are bent.
- **5.4(i):** Blacken the four circles carrying NO ligands: label the upper iron **A**, then the three basal irons **B, C, D from left to right**. This is **Roussin's black salt anion**, $[\text{Fe}_4\text{S}_3(\text{NO})_7]^-$, with coordination SMILES:

```
[Fe+]12456(<-N#[O+])<-[S-2]3->[Fe-]-4(<-N#[O+])(<-N#[O+])<-[S-2]->1->[Fe-]-5(<-N#[O+])(<-N#[O+])<-[S-2]->2->[Fe-]-6<-3(<-N#[O+])<-N#[O+]
```

- **5.4(ii):** In the conventional localized bonding model,



The corresponding formal oxidation states are +1, –1, –1, –1.

- **5.5(i): Roussin's red salt anion**, $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$: an alternating four-membered Fe–S–Fe–S ring, with two terminal N-bound NO ligands on each iron and an Fe–Fe bond across the ring. Coordination SMILES:

```
[S-2]1->[Fe-]2(<-N#[O+])(<-N#[O+])<-[S-2]->[Fe-]2<-1(<-N#[O+])<-N#[O+]
```

- **5.5(ii):** Each iron has oxidation state –1.
- **5.5(iii):** Add **two methyl cations**, CH_3^+ , [CH3+], formally one at each sulfur. $n = 0$. The product is **Roussin's red salt methyl ester**, $[\text{Fe}_2(\text{SCH}_3)_2(\text{NO})_4]$, with coordination SMILES:

```
C[S-]1->[Fe-]2(<-N#[O+])(<-N#[O+])<-[S-](C)->[Fe-]2<-1(<-N#[O+])<-N#[O+]
```

Solution

5.1

Nitric oxide has $5 + 6 = 11$ valence electrons. Its valence molecular-orbital occupation is

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1.$$

The highest occupied level is the doubly degenerate antibonding π^* level, containing just one electron:



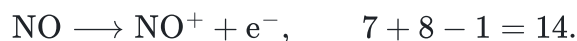
Thus the HOMO is singly occupied, while the other spatial orbital of the same π^* pair is vacant. The choice of which member contains the electron is arbitrary.

5.2

Carbon monoxide, CO, $[C^-]\#[O^+]$, has

$$6 + 8 = 14 \text{ total electrons.}$$

Neutral nitric oxide has $7 + 8 = 15$. Removing one electron therefore produces the isoelectronic nitrosonium ion:



Equivalently, both carbon monoxide and nitrosonium have ten valence electrons. Consequently, **option b**, NO^+ , is the required formal description of the coordinated ligand.

5.3

Peroxynitrous acid has the connectivity

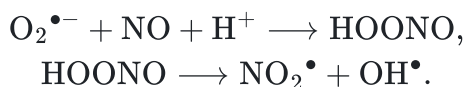


The relevant electron-domain counts are:

- At nitrogen: one double bond, one single bond and one lone pair give three electron domains. The electron-domain arrangement is approximately trigonal planar, and the $O=N-O$ bond angle is bent.
- At the oxygen between nitrogen and the hydroxyl oxygen: two single bonds and two lone pairs give four electron domains. The electron-domain arrangement is approximately tetrahedral, and the $N-O-O$ angle is also bent.

The ideal reference angles for these electron-domain arrangements are 120° and 109.5° , respectively; the problem does not supply exact molecular bond angles. **Only B shows both required bends.** Its SMILES gives connectivity, without selecting a particular torsional conformation.

The balanced reaction sequence is



The additional species are the **superoxide radical anion**, $[O^-][O]$; a **proton**, $[H^+]$; the **nitrogen dioxide radical**, $O=[N^+][O^-]$; and the **hydroxyl radical**, $[OH]$.

Homolytic cleavage of the peroxide $O-O$ bond gives one electron to each fragment, producing the two radicals.

5.4(i)

Identify each iron by its directly attached NO ligand or ligands:

Label	Circle to blacken	Ligands attached to that iron
Fe(A)	Upper central circle, immediately below the vertical NO group	One NO and three sulfurs
Fe(B)	Left basal circle, carrying leftward and downward NO groups	Two NO and two sulfurs
Fe(C)	Lower central/front circle, carrying the short rightward and downward-left NO groups	Two NO and two sulfurs
Fe(D)	Right basal circle, carrying rightward and downward NO groups	Two NO and two sulfurs

The remaining three core atoms are bridging **sulfide ions**, formally S^{2-} , [S-2]. Each bridges three irons. Their connections are:

$$(A, B, C), \quad (A, B, D), \quad (A, C, D).$$

Thus A is bonded to all three sulfurs, while each basal iron is bonded to two. Each NO binds through nitrogen, with approximately linear Fe–N–O geometry. The four ligand directions at each iron form a distorted tetrahedral arrangement.

5.4(ii)

The printed *sp* assumption appears to require correction to *sp*³ to describe these four ligand directions.

Using the formal nitrosonium and sulfide assignments, charge balance gives

$$\sum_i x_i + 3(-2) + 7(+1) = -1,$$

so

$$\sum_i x_i = -2, \quad \bar{x} = -0.5.$$

Iron is a group-8 element, so an iron with formal oxidation state x has the d -electron count

$$d^{8-x}.$$

The conventional localized bonding description has three Fe–Fe bonds: A–B, A–C and A–D. Each iron receives eight electrons from its four ligand donor pairs; each Fe–Fe bond contributes one electron to the count at either end.

Applying the 18-electron count gives, for A,

$$(8 - x_A) + 8 + 3 = 18 \implies x_A = +1, \quad d_A^7.$$

For each basal iron,

$$(8 - x_{\text{basal}}) + 8 + 1 = 18 \implies x_{\text{basal}} = -1, \quad d_{\text{basal}}^9.$$

The mean oxidation number is therefore

$$\frac{(+1) + 3(-1)}{4} = -0.5,$$

as required. The formal $3d$ -orbital occupations before pairing through the metal–metal interactions are

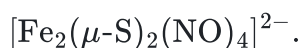
$$\begin{aligned} A : \quad 3d^7 : & \quad [\uparrow\downarrow][\uparrow\downarrow][\uparrow][\uparrow][\uparrow], \\ B, C, D : \quad 3d^9 : & \quad [\uparrow\downarrow][\uparrow\downarrow][\uparrow\downarrow][\uparrow\downarrow][\uparrow]. \end{aligned}$$

These are local electron-counting descriptions, rather than a claim that the complete cluster has six independent unpaired electrons.

5.5(i)

Draw a four-membered ring with iron atoms at two opposite vertices and sulfurs at the other two. Both sulfurs bridge both irons. Attach two terminal, N-bound NO ligands to each iron and show the conventional Fe–Fe bond joining the opposite iron vertices.

This gives the connectivity



The four-membered ring drawing specifies connectivity; the coordination SMILES does not fix the three-dimensional geometry.

5.5(ii)

The two equivalent iron atoms have oxidation state x . With two sulfides and four nitrosonium ligands,

$$2x + 2(-2) + 4(+1) = -2.$$

Hence

$$2x = -2 \implies \boxed{x = -1}.$$

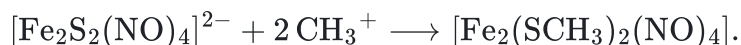
Each iron consequently has nine d electrons. Its electron count, including the Fe–Fe bond, is

$$9 + 4(2) + 1 = 18.$$

5.5(iii)

Each bridging sulfide undergoes methylation to become a bridging **methanethiolate ligand**, SCH_3^- , $\text{C}[S-]$. Formation of the S–C bond uses a sulfur lone pair and an electrophilic methyl group, represented among the choices by CH_3^+ .

The balanced formal methylation equation is



The resulting charge is

$$n = -2 + 2(+1) = \boxed{0}.$$

The same result follows from the product's ligand charges, with both iron oxidation states unchanged:

$$n = 2(-1) + 2(-1) + 4(+1) = 0.$$

The solution was checked against the official solution.

Problem 6: The surfactant AOT and micellar extraction of proteins

A surfactant molecule can generally be modelled as Fig. 1 where a circle presents the polar head (PH), i.e. the hydrophilic part of the molecule, and a rectangle represents the non-polar tail (NT), i. e. the hydrophobic part of the molecule.

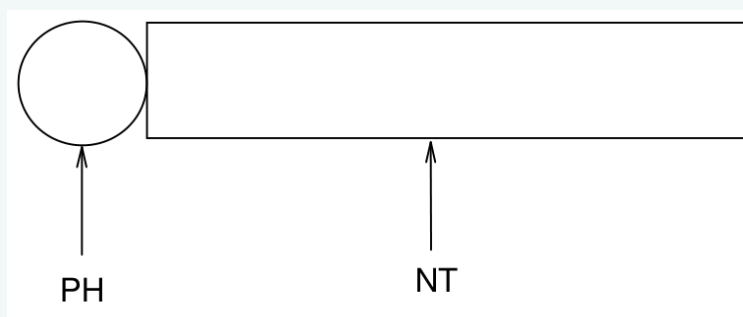


Fig. 1

6.1 AOT is a surfactant. Its systematic name (IUPAC name) is sulfobutanedioic acid 1,4-bis-(2-ethylhexyl) ester sodium salt (formula $\text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$).

i) Write the structural formula for AOT and fill its PH and NT in the circle and rectangle on your answer sheet.

ii) Choose the type of surfactant AOT among the following.

a) Non-ionic; b) Anionic; c) Cationic; d) Others.

6.2 Mixing an aqueous solution of 50 mmol AOT with isooctane (volume ratio 1 : 1), a micellar extraction system will be formed in the isooctane phase (organic phase).

i) Using the model as shown in Fig. 1, draw a micelle with 10 AOT molecules under the given condition.

ii) What species are in the inner cavity of this micelle? Write their chemical formulas.

6.3 There is an aqueous solution containing the proteins as listed below:

Protein	Molecular mass (M_r) $\times 10^4$	Isoelectric point (PI)
A	1.45	11.1
B	1.37	7.8
C	6.45	4.9
D	6.80	4.9
E	2.40	4.7
F	2.38	0.5

The separation of proteins can be performed by mixing the AOT micellar extraction system with the solution. Adjusting the pH value of the solution to 4.5, only three of the above listed six proteins can be extracted into the micelles. Which proteins will be extracted?

6.4 The three proteins entered into the micelles will be separated from each other by the following procedure shown as in Fig. 2. Each extracted protein can be sequentially transported into a respective water phase.

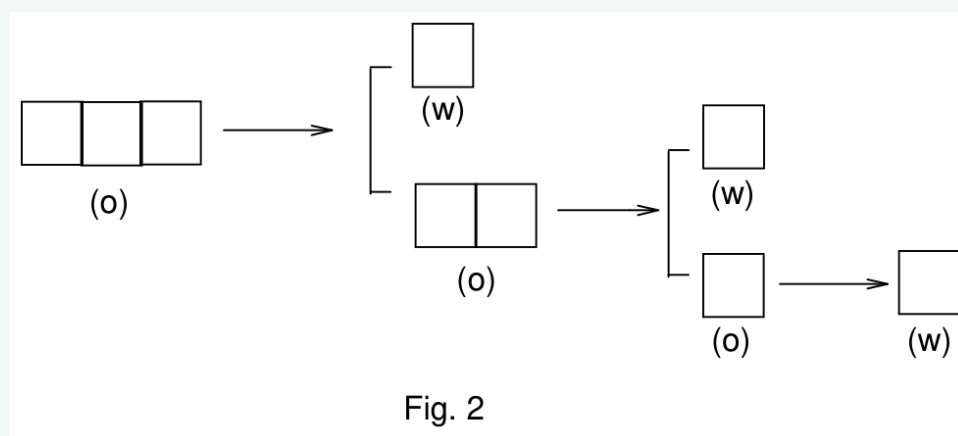


Fig. 2

Note: (w) represents water phase; (o) represents organic phase

Fill the three extracted proteins in the left boxes first and then separate them by the procedure given, and give the separation conditions above each arrow as well.

Official English text of the problem.

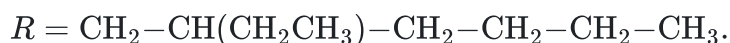
Answers

- **6.1(i)** AOT is **sodium bis(2-ethylhexyl) sulfosuccinate**, SMILES: CCCCC(CC)COC(=O)CC(S(=O)(=O)[O-])C(=O)OCC(CC)CCCC.[Na+]. Its PH is the sulfonate-containing polar core; its NT consists of the two 2-ethylhexyl hydrocarbon chains.
- **6.1(ii) b) Anionic.**
- **6.2(i)** Draw a **reverse micelle**: ten polar-head circles surrounding an aqueous cavity, with ten tail rectangles extending radially outward into isooctane.
- **6.2(ii) Water**, H_2O , SMILES O, and **sodium ions**, Na^+ , SMILES [Na+].
- **6.3** Proteins **A, B and E**.
- **6.4** Release **E**, then **B**, then **A** into separate aqueous phases. Suitable successive conditions are $4.7 < \text{pH} < 7.8$, then $7.8 < \text{pH} < 11.1$, then $\text{pH} > 11.1$; for example, **pH 6.0, 9.0 and 12.0**, respectively.

Solution

6.1(i) Structure and hydrophilic/hydrophobic regions

Let R denote a 2-ethylhexyl group:



The condensed structural formula of AOT is



The two ester groups each carry a 2-ethylhexyl chain, and the sulfonate group is bonded directly to a central carbon. The two R groups contribute 16 carbon atoms; the central skeleton contributes four, giving the stated formula $\text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$.

For the model on the answer sheet:

- **Circle, PH:** put the sulfonate-containing polar region here. The principal ionic hydrophilic group is the attached sulfonate, $-\text{SO}_3^-$, fragment SMILES [*]S(=O)(=O)[O-]. The ester groups also contribute polarity. Sodium is its counterion.
- **Rectangle, NT:** put the two 2-ethylhexyl groups here, each represented by fragment SMILES [*]CC(CC)CCCC. These hydrocarbon chains constitute the hydrophobic region.

Here [*] marks attachment to the remainder of the molecule. Although AOT has two hydrocarbon chains, the problem's simplified model represents its entire non-polar region by one rectangle.

No stereochemical configuration is specified, so the AOT SMILES leaves stereochemistry unspecified.

6.1(ii) Surfactant classification

The amphiphilic organic ion bears a negatively charged sulfonate group. The positive sodium ion is the counterion. Therefore AOT is an **anionic surfactant**, option **b**.

6.2(i) Arrangement in the organic phase

Isooctane is **2,2,4-trimethylpentane**, C_8H_{18} , SMILES CC(C)(C)CC(C)C. It is a non-polar solvent, so the hydrocarbon tails are directed into this continuous organic phase. The polar heads gather around entrapped water, forming a **reverse micelle**.

Describe the required drawing as follows:

- Place exactly **ten circles** around a central aqueous cavity, approximately 36° apart.
- Attach one rectangle to the outward-facing side of each circle.
- Direct all ten rectangles radially away from the cavity into the surrounding isooctane.

Thus the negatively charged heads line the inner aqueous surface, and the non-polar tails form the exterior.

6.2(ii) Contents of the cavity

The cavity contains **water, H_2O , and hydrated sodium counterions, Na^+** . The polar environment accommodates these ions, while the attached sulfonate groups line the cavity's boundary.

The amount of water enclosed is not specified.

6.3 Selection of proteins

The table's PI denotes the **isoelectric point**, conventionally written pI . The relevant charge relationships are

$$\begin{aligned} pH < pI &\Rightarrow \text{net positive protein charge,} \\ pH = pI &\Rightarrow \text{zero net protein charge,} \\ pH > pI &\Rightarrow \text{net negative protein charge.} \end{aligned}$$

AOT's inward-facing heads are negatively charged, so they attract positively charged proteins. Entry also requires a protein to fit within the micellar aqueous region.

At pH 4.5:

Protein	M_r	Net charge	Consequence in the intended model
A	1.45×10^4	Positive	Attracted and sufficiently small
B	1.37×10^4	Positive	Attracted and sufficiently small
C	6.45×10^4	Positive	Excluded because of its larger size
D	6.80×10^4	Positive	Excluded because of its larger size
E	2.40×10^4	Positive	Attracted and sufficiently small
F	2.38×10^4	Negative	Electrostatically disfavoured

Protein F has $pH > pI$, so its charge has the same sign as the AOT heads. Proteins A–E all have the favourable positive charge, but C and D have much greater molecular masses than A, B and E.

Using this size distinction together with the stated fact that exactly three proteins enter the micelles gives

A, B and E.

6.4 Sequential back-extraction

Raise the pH in stages. When the pH exceeds a protein's pI , its net charge becomes negative, favouring its release from the negatively charged micellar interior into the external aqueous phase.

The three relevant isoelectric points are

$$pI_E = 4.7 < pI_B = 7.8 < pI_A = 11.1.$$

Fill the three initial organic-phase boxes, from left to right, with **A, B, E**. Complete the remaining boxes and arrow conditions as follows:

Arrow	Aqueous-phase condition	Protein in the new water-phase box, (w)	Proteins remaining in the organic-phase boxes, (o)
First	$4.7 < \text{pH} < 7.8$, e.g. 6.0	E	A, B
Second	$7.8 < \text{pH} < 11.1$, e.g. 9.0	B	A
Third	$\text{pH} > 11.1$, e.g. 12.0	A	None

At the first stage, E is negative while A and B remain positive. At the second stage, B becomes negative while A remains positive. At the final stage, A also becomes negative.

After each equilibration, separate and collect the aqueous phase before contacting the remaining organic phase with the next aqueous solution.

The solution was checked against the official solution.