[Marking Scheme] Rapid and Visual Nucleic Acid Testing for COVID-19

1.1 (1.0 pt)

(d)

1.2 (1.0 pt)

(a)

1.3 (4.0 pt)

The volume of a gold nanoparticle: 1 point

$$V_{NP} = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 = \frac{4}{3} \times 3.14 \times \left(\frac{30.0 \times 10^{-7}}{2}\right)^3 = 1.41 \times 10^{-17}\ \text{cm}^3 \text{ or } 1.41 \times 10^{-23}\ \text{m}^3$$

The mass of a gold nanoparticle: 1 point

$$m_{NP} = \rho V_{NP} = 19.3 \times 1.41 \times 10^{-17} = 2.72 \times 10^{-16}\ \text{g}$$

The number of gold atoms in each particle: 2 point

$$N = \frac{m_{NP}}{AW_{Au}} \cdot N_A = \frac{2.72 \times 10^{-16}}{197.0} \times 6.022 \times 10^{23} = 8.31 \times 10^5$$

OR 4 points

$$N = \frac{V_{NP}}{V_{\text{atom}}} = \frac{\pi\rho N_A D^3}{6M} = \frac{3.14 \times 19.3 \times 6.022 \times 10^{23} \times (30.0 \times 10^{-7})^3}{6 \times 197.0} = 8.34 \times 10^5$$

OR

The volume of a gold nanoparticle: 1 point

$$V_{NP} = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 = \frac{4}{3} \times 3.14 \times \left(\frac{30.0 \times 10^{-7}}{2}\right)^3 = 1.41 \times 10^{-17}\ \text{cm}^3 \text{ or } 1.41 \times 10^{-23}\ \text{m}^3$$

The mass of each gold atom: 1 point

$$m = \frac{AW_{Au}}{N_A} = \frac{197.0}{6.022 \times 10^{23}} = 3.271 \times 10^{-22}\ \text{g}$$

The volume of each gold atom: 1 point

$$V_{\text{atom}} = \frac{m}{\rho} = \frac{3.271 \times 10^{-22}}{19.3} = 1.69 \times 10^{-23}\ \text{cm}^3$$

The number of gold atoms in each particle: 1 point

$$N = \frac{V_{NP}}{V_{\text{atom}}} = \frac{1.41 \times 10^{-17}}{1.69 \times 10^{-23}} = 8.34 \times 10^5$$

4 points in total

−1 point for calculating error.

1.4 (4.0 pt)

The total number of gold atoms: 1 points

$$N_{\text{Total}} = \frac{5.2\times10^{-3}}{394}\times 6.022\times10^{23} = 7.9\times10^{18}$$

The concentration of gold nanoparticles: 2 points

$$C = \frac{N_{\text{Total}}}{NVN_A} = \frac{7.9\times10^{18}}{8.34\times10^{5}\times100\times10^{-3}\times6.022\times10^{23}} = 1.6\times10^{-10}\ \text{mol L}^{-1}$$

The extinction coefficient: 1 points

$$\varepsilon = \frac{A}{lC} = \frac{0.800}{1\times1.6\times10^{-10}} = 5.0\times10^{9}\ \text{L mol}^{-1}\ \text{cm}^{-1}$$

4 points in total

−1 point for each calculating error.

1.5 (4.0 pt)

$$A_1 = \varepsilon l C_1 = \varepsilon l\frac{0.10C_x}{1.0} = 0.400$$ 1 point

$$A_2 = \varepsilon l C_2 = \varepsilon l\frac{0.10C_x + 2.0\times0.10}{1.0} = 0.900$$ 1 point

OR

$$\frac{0.400}{0.900} = \frac{\frac{0.10C_x}{1.0}}{\frac{0.10C_x+2.0\times0.10}{1.0}}$$ 2 points

$C_x = 1.6\ \mu\text{g mL}^{-1}$ 2 points

4 points in total

−1 point for calculating error.

[Marking Scheme] Chromium in Ancient and Modern Times

2.1 (2.0 pt)

A: 8 B: 16

2 points in total, each correct assignment 1 point

2.2 (1.0 pt)

Fe (or iron)

2.3 (6.0 pt)
$Fe^{3+}: 7,\ Cr^{3+}: 9$
Solution 1:
Assume there are x Fe ions (including Fe^{2+} and Fe^{3+}) and y Cr^{3+} ions in a cubic cell, then

$$\frac{x}{y} = \frac{63.6 \times (52.00 \times 2 + 16.00 \times 3)}{36.4 \times (55.85 \times 2 + 16.00 \times 3)}$$

which gives the result: $\frac{x}{y} = 1.66$
Considering that the total amount of the cations in each crystal cell is 24, it can be obtained

$$(1 + 1.66)y = 24$$

which gives the result: $y \approx 9$
Thus, the amount of Fe^{3+} occupying the octahedral vacancies is

$$16 - 9 = 7$$

Solution 2:
Assume there are x Fe ions (including Fe^{2+} and Fe^{3+}) in the final compound, then, the number of Cr^{3+} should be $3-x$ because the summary of A+B should be 3 in AB_2O_4, and the formula of the compound should be $Fe_xCr_{3-x}O_4$, then

$$\frac{x}{3-x} = \frac{63.6 \times (52.00 \times 2 + 16.00 \times 3)}{36.4 \times (55.85 \times 2 + 16.00 \times 3)} = \frac{5}{3}$$

which gives the result: $x = 1.875$
Accordingly, Fe^{2+} in the tetrahedral vacancies is 1, and the number of Fe^{3+} in the octahedral vacancies is

$$x - 1 = 1.875 - 1 = 0.875$$

and the number of Cr^{3+} occupying the octahedral is

$$3 - x = 3 - 1.875 = 1.125$$

In one unit cell, there are 8 Fe^{2+}, thus the numbers of Fe^{3+} and Cr^{3+} are

$$\frac{8}{1} \times 0.875 = 7 \quad \text{and} \quad \frac{8}{1} \times 1.125 = 9$$

respectively.
6 points in total
2 points for the correct molar ratio of Fe/Cr
1 point for the correct result of the amount of Cr^{3+}
1 point for the correct result of the total amount of Fe
1 point for the correct result of the amount of Fe^{3+}
1 point for the correct result of the number of Fe^{3+} and Cr^{3+} in the **B** sites of one unit cell

2.4 (1.0 pt)

Na_2CrO_4

2.5 (2.0 pt)

$Na_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + H_2O + 2NaHSO_4$

Ionic form is acceptable.
-1 point if the stoichiometry is incorrect.

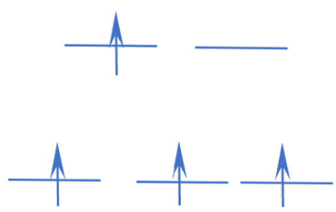
2.6 (1.0 pt)

(A)

2.7 (1.0 pt)

(B)

2.8 (5.0 pt)



CFSE $= 0 - E_{\text{octa}} = 0 - [(-2/5\Delta_o) \times 3 + 3/5\Delta_o] = 3/5\Delta_o = 9600$ cm^{-1}

5 points in total

1 point for the correct energy level of the five 3*d* orbitals in octahedral crystal field.

1 point for the correct electron configuration on the energy level lines.

1 point for the correct equation of CFSE.

1 point for the result of CFSE with Δ_o.

1 point for the result of CFSE with cm^{-1}.

2.9 (2.0 pt)
$\mu = \sqrt{4(4+2)}\,\mu_\mathrm{B} = 4.9\,\mu_\mathrm{B}$

2 points

[Marking Scheme] Capture and Transformation of Carbon Dioxide

3.1 (2.0 pt)
A: $CaCO_3$ **B**: CaO
2 points in total; 1 point for each

3.2 (5.0 pt)

step 1: (2a) $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

or $2OH^- + CO_2 \longrightarrow CO_3^{2-} + H_2O$

(2b) $NaOH + CO_2 \longrightarrow NaHCO_3$

or $OH^- + CO_2 \longrightarrow HCO_3^-$

or $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

or $CO_3^{2-} + CO_2 + H_2O \longrightarrow 2HCO_3^-$

step 2: (2c) $Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$

(2d) $NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + NaOH + H_2O$

step 3: (2e) $CaCO_3 \longrightarrow CaO + CO_2$

5 points in total; 1 point for each equation (2a) $\sim$ (2e)

3.3 (2.0 pt)

A: $H_2 \rightarrow 2H^+ + 2e^-$

C: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

2 points in total; 1 point for each equation

3.4 (3.0 pt)

1 $H^+ + CO_3^{2-} \longrightarrow HCO_3^-$

2 $H^+ + HCO_3^- \longrightarrow H_2CO_3$

3 $H_2CO_3 \longrightarrow H_2O + CO_2$

3 points in total; 1 point for each equation.

3.5 (2.0 pt)

[✓] (a) [ ] (b) [ ] (c) [✓] (d) [ ] (e)

2 points in total; 1 point for each correct selection.

If wrong item(s) is/are included, −1 point for each till the total point is zero, no negative score.

3.6 (8.0 pt)

Rate of H^+ production:

$r(H^+) = 60\ \text{s min}^{-1} \times 2.00\ \text{A}/(96485\ \text{C mol}^{-1})$ — 2 points

$= 1.24 \times 10^{-3}\ \text{mol min}^{-1} = 1.24\ \text{mmol min}^{-1}$ — 1 point

Input rate of HCO_3^- to zone B:

$r(HCO_3^-) = 0.10\ \text{mol L}^{-1} \times 10.0\ \text{mL min}^{-1} = 1.0\ \text{mmol min}^{-1}$

Input rate of CO_3^{2-} to zone B:

$r(CO_3^{2-}) = 0.050\ \text{mol L}^{-1} \times 10.0\ \text{mL min}^{-1} = 0.50\ \text{mmol min}^{-1}$ — 1 point

$H^+ + CO_3^{2-} \longrightarrow HCO_3^-$ $H^+ + HCO_3^- \longrightarrow CO_2 + H_2O$

The amount of dissolved CO_2 in the flow:

$10.0\ \text{mL min}^{-1} \times 0.033\ \text{mol L}^{-1} = 0.33\ \text{mmol min}^{-1}$ — 1 point

Rate of CO_2 production:

$r(CO_2) = r(H^+) - r(CO_3^{2-}) - 0.33\ \text{mmol min}^{-1}$ — 2 points

$= 1.24\ \text{mmol min}^{-1} - 0.50\ \text{mmol min}^{-1} - 0.33\ \text{mmol min}^{-1} = 0.41\ \text{mmol min}^{-1}$ — 1 point

8 points in total

Some of the steps in the derivation and in the calculation may be taken implicitly or simultaneously. As long as they are correct, full marks will be scored for each of the partial steps.

3.7 (2.0 pt)

$Zn_{24}(C_4H_5N_2)_{36}^{12+}$ or $Zn_{24}(C_4H_5N_2)_{60}^{12-}$

2 points in total

Expression $Zn_{24}(mIm)_{36}^{12+}$ or $Zn_{24}(mIm)_{60}^{12-}$ is acceptable.

3.8 (2.0 pt)

$Zn_{12}(C_4H_5N_2)_{24}$

2 points in total

Expression $Zn_{12}(mIm)_{24}$ or $Zn_{12}C_{96}H_{120}N_{48}$ is acceptable.

3.9 (5.0 pt)

$$M_{Zn(C_4H_5N_2)_2} = [65.38 + (12.01 \times 4 + 1.01 \times 5 + 14.02 \times 2) \times 2]\ \text{g mol}^{-1} = 227.6\ \text{g mol}^{-1}$$ 1 point

$$S = \frac{2 \times 4\pi r^2 \times N_A \times 1\ \text{g}}{12 \times M_{Zn(C_4H_5N_2)_2}}$$

$$= \frac{2 \times 4 \times 3.14 \times \left(\frac{1.16 \times 10^{-9}\ \text{m}}{2}\right)^2 \times 6.02 \times 10^{23}\ \text{mol}^{-1} \times 1\ \text{g}}{12 \times [65.38 + (12.01 \times 4 + 1.01 \times 5 + 14.01 \times 2) \times 2]\ \text{g mol}^{-1}}$$

$$= \frac{50.8 \times 10^5}{12 \times 227.6}\text{m}^2 = 1.86 \times 10^3\ \text{m}^2$$

4 points: 2 point for the correct formula (1 point for the coefficient 2), 1 for properly introducing data, 1 for correct calculation result.

5 points in total.

Some of the steps in the derivation and in the calculation may be taken implicitly or simultaneously. As long as they are correct, full marks will be scored for each of the partial steps.

3.10 (7.0 pt)

Volume of one spherical cage:

$$V_{\text{Cage}} = (4/3) \times 3.14 \times (1.16\ \text{nm}/2)^3 = 0.817\ \text{nm}^3$$ 1 point

Volume of the unit cell:

$$V_{\text{cell}} = (1.632\ \text{nm})^3 = 4.347\ \text{nm}^3$$ 1 point

Porosity:

$$R = 2 \times V_{\text{Cage}}/V_{\text{cell}} = 2 \times 0.817\ \text{nm}^3/4.347\ \text{nm}^3 = 0.376$$ 2 points

1 point for the coefficient 2

$$V_{\text{p}} = \frac{2 \times V_{\text{cage}} \times N_{\text{A}} \times 1\ \text{g}}{12 \times M_{\text{Zn(C}_4\text{H}_5\text{N}_2)_2}} = \frac{\frac{4}{3}\pi r^3 \times N_{\text{A}} \times 1\ \text{g}}{6 \times M_{\text{Zn(C}_4\text{H}_5\text{N}_2)_2}}$$

$$= \frac{0.817 \times 10^{-21}\ \text{cm}^3 \times 6.02 \times 10^{23}\ \text{mol}^{-1} \times 1\ \text{g}}{6 \times 227.6\ \text{g mol}^{-1}} = 0.360\ \text{cm}^3$$ 3 points

3 points: 1 for the correct formula, 1 for properly introducing data; 1 for correct calculation result

7 points in total.

Some of the steps in the derivation and in the calculation may be taken implicitly or simultaneously. As long as they are correct, full marks will be scored for each of the partial steps.

3.11 (2.0 pt)

I (b) **II** (d)

2 points in total, 1 point for each correct selection.

3.12 (2.0 pt)

$Zn(C_4H_5N_2)_2 + CO_2 + H_2O \longrightarrow ZnCO_3 + 2C_4H_6N_2$

or $Zn(mIm)_2 + CO_2 + H_2O \longrightarrow ZnCO_3 + 2HmIm$

2 points in total

[Marking Scheme] A New Journey for Ancient Sulfur

4.1 (2.0 pt)

$3\,FeS_2 + 2\,O_2 \xrightarrow{\Delta} 6\,S + Fe_3O_4$ or $12\,FeS_2 + 8\,O_2 \xrightarrow{\Delta} 3\,S_8 + 4\,Fe_3O_4$

No penalty will be given if the heating symbol on the reaction arrow is missing.
−1 point if the stoichiometry is incorrect.

4.2 (4.0 pt)

(a) $Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$ (2 points)

or

$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2I^-$

(b) $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$ (2 points)

or

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

No partial point will be given if NaOH is present for (a).
No partial point will be given if the oxidation product is not $Na_2S_4O_6$ or $S_4O_6^{2-}$ for (b).
−1 point if the stoichiometry is incorrect for each equation.

4.3 (4.0 pt)

$0.05122\ \text{mol L}^{-1} \times 50.00\ \text{mL} = 2.561\ \text{mmol}$ (1 point)

$\frac{1}{2} \times 0.1012\ \text{mol L}^{-1} \times 18.47\ \text{mL} = 0.9346\ \text{mmol}$ (1 point)

$(2.561\ \text{mmol} - 0.9346\ \text{mmol}) \times 10^{-3} \times 20 \times 32.06\ \text{g mol}^{-1} = 1.043\ \text{g}$ (1 point)

$\frac{1.043\ \text{g}}{(1.043\ \text{g} + 17.6\ \text{g})} \times 100\% = 5.59\%$ (1 point)

4 points in total
For each calculation, consider whether the logic for solving this question is correctly established;
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.
If the calculation is based on the incorrect equation answered in 4.2 (b), no penalty will be given when the calculation is correct.

4.4 (3.0 pt)

(a) $S_8 + 16Li^+ + 16e^- \longrightarrow 8Li_2S$ (2 points)

(b) $Li \longrightarrow Li^+ + e^-$ or $16Li \longrightarrow 16Li^+ + 16e^-$ (1 point)

3 points in total
No partial point will be given if the cathode and anode reactions are reversed.
-1 point if the stoichiometry is incorrect for (a).
No penalty will be given if the equation is written as $S + 2e^- \longrightarrow S^{2-}$ for (a).
No penalty will be given if the equation is written as $S + 2Li^+ + 2e^- \longrightarrow Li_2S$ for (a).
No penalty will be given if e^- is written as e.

4.5 (1.0 pt)

$$\frac{8 \times 32.06}{16 \times 6.941} = 2.3$$

1 point in total
0.5 point will be given if the ratio is presented in reverse order.
No penalty will be given if the ratio is in reverse order but the cathode and the anode are correctly identified.

4.6 (5.0 pt)

The total energy of the LIB is $3.8\,\text{V} \times 3.110\,\text{A h} \times 3600\,\text{s/h} = 4.25 \times 10^4\,\text{J}$ (1 point)

Energy consumed by the mobile phone per hour is $\dfrac{4.25 \times 10^4\,\text{J}}{22\,\text{h}} = 1.93 \times 10^3\,\text{J h}^{-1}$ (1 point)

The capacity of the ideal lithium-sulfur battery pack is

$$\frac{23\,\text{g} \times 16 \times 96485\,\text{C mol}^{-1}}{8 \times 32.06\,\text{g mol}^{-1}} = \frac{23\,\text{g} \times 2 \times 96485\,\text{C mol}^{-1}}{32.06\,\text{g mol}^{-1}} = 1.4 \times 10^5\,\text{C}$$ (1 point)

The total energy of the ideal lithium-sulfur battery pack is

$4.2\,\text{V} \times 1.4 \times 10^5\,\text{C} = 5.9 \times 10^5\,\text{J}$ (1 point)

After a full charge, the new battery pack can provide energy for the phone to play videos continuously for: $\dfrac{5.9 \times 10^5\,\text{J}}{1.93 \times 10^3\,\text{J h}^{-1}} = 306\,\text{h}$ (1 point)

5 points in total
For each calculation, consider whether the logic for solving this question is correctly established;
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.
−1 point if any other unit than asked unit is used in the answer.
No penalty will be given if the result is 301 h without rounded calculations.

4.7 (2.0 pt)

$(2n - 2)\,\text{Li} + \text{Li}_2\text{S}_n \longrightarrow n\text{Li}_2\text{S}$

−1 point if the stoichiometry is incorrect.
No penalty will be given if n is written as 3-8 and the stoichiometry is correct.

4.8 (4.0 pt)

$Li_2S_6(\mathrm{I})(\mathrm{DME}) \longrightarrow Li_2S_6(\mathrm{II})(\mathrm{DME})$

$\Delta G^{\ominus}_{\mathrm{I}\longrightarrow\mathrm{II}} = \Delta G^{\ominus}_{\mathrm{d1}}(\mathrm{I}) - \Delta G^{\ominus}_{\mathrm{d1}}(\mathrm{II}) = 20.68\ \mathrm{kJ\,mol^{-1}} - 18.92\ \mathrm{kJ\,mol^{-1}} = 1.76\ \mathrm{kJ\,mol^{-1}}$

or

$\Delta G^{\ominus}_{\mathrm{I}\longrightarrow\mathrm{II}} = \Delta G^{\ominus}_{\mathrm{dr}}(\mathrm{I}) - \Delta G^{\ominus}_{dr}(\mathrm{II}) = 45.13\ \mathrm{kJ\,mol^{-1}} - 43.37\ \mathrm{kJ\,mol^{-1}} = 1.76\ \mathrm{kJ\,mol^{-1}}$ (1 point)

$\Delta G^{\ominus}_{\mathrm{I}\longrightarrow\mathrm{II}} = -RT \ln K^{\ominus}_{\mathrm{I}\longrightarrow\mathrm{II}}$ (1 point)

$K^{\ominus}_{\mathrm{I}\longrightarrow\mathrm{II}} = \exp\left(-\frac{1.76\ \mathrm{kJ\,mol^{-1}} \times 1000}{8.314\ \mathrm{J\,mol^{-1}\,K^{-1}} \times 298.15\ \mathrm{K}}\right) = 0.492$ (1 point)

$K^{\ominus}_{\mathrm{I}\longrightarrow\mathrm{II}} = \frac{[Li_2S_6(\mathrm{II})]/c^{\ominus}}{[Li_2S_6(\mathrm{I})]/c^{\ominus}} = \frac{[Li_2S_6(\mathrm{II})]}{[Li_2S_6(\mathrm{I})]} = 0.492$ (1 point)

4 points in total
For each calculation, consider whether the logic for solving this question is correctly established;
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.

4.9 (5.0 pt)

$\frac{[Li_2S_6(II)]}{[Li_2S_6(I)]}$ =0.492, $[Li_2S_6(II)]$ =0.492$[Li_2S_6(I)]$

$Li_2S_6 \longrightarrow Li^+ + LiS_6^-$

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{[Li_2S_6]} = \frac{[Li^+][LiS_6^-]}{[Li_2S_6(I)] + [Li_2S_6(II)]}$$ (1 point)

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{1.492[Li_2S_6(I)]} = \frac{K_{d1}^{\ominus}(I)}{1.492}$$ (1 point)

or

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{3.03[Li_2S_6(II)]} = \frac{K_{d1}^{\ominus}(II)}{3.03}$$

or

$$K_{d1}^{\ominus} = \frac{[Li^+][LiS_6^-]}{[Li_2S_6(I)] + [Li_2S_6(II)]} = \frac{1}{\frac{1}{K_{d1}^{\ominus}(I)} + \frac{1}{K_{d1}^{\ominus}(II)}}$$

$Li_2S_6(I) \longrightarrow Li^+ + LiS_6^-$, $\Delta G_{d1}^{\ominus}(I) = -RT \ln K_{d1}^{\ominus}(I)$ (1 point)

$$K_{d1}^{\ominus}(I) = \exp\left(-\frac{20.68\,\text{kJ mol}^{-1} \times 1000}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\text{K}}\right) = 2.37 \times 10^{-4}$$ (1 point)

or

$Li_2S_6(II) \longrightarrow Li^+ + LiS_6^-$, $\Delta G_{d1}^{\ominus}(II) = -RT \ln K_{d1}^{\ominus}(II)$

$$K_{d1}^{\ominus}(II) = \exp\left(-\frac{18.92\,\text{kJ mol}^{-1} \times 1000}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\text{K}}\right) = 4.84 \times 10^{-4}$$

$$K_{d1}^{\ominus} = \frac{2.37 \times 10^{-4}}{1.492} = 1.59 \times 10^{-4}$$ (1 point)

or

$$K_{d1}^{\ominus} = \frac{4.84 \times 10^{-4}}{3.03} = 1.59 \times 10^{-4}$$

or

$$K_{d1}^{\ominus} = \frac{1}{\frac{1}{K_{d1}^{\ominus}(I)} + \frac{1}{K_{d1}^{\ominus}(II)}} = \frac{1}{\frac{1}{2.37 \times 10^{-4}} + \frac{1}{4.84 \times 10^{-4}}} = 1.59 \times 10^{-4}$$

5 points in total

For each calculation, consider whether the logic for solving this question is correctly established; If not, no points will be given.

-1 point if the answer is not correct due to miscalculation.

4.10 (4.0 pt)

$$[Li_2S_6] > [LiS_6^-] > [LiS_3^\bullet] > [S_6^{2-}]$$

$LiS_6^-(DME) \longrightarrow Li^+(DME) + S_6^{2-}(DME)$

$\Delta G_{d2}^\ominus = -RT \ln K_{d2}^\ominus$, $K_{d2}^\ominus = \exp\left(-\frac{100.55\ kJ\ mol^{-1} \times 1000}{8.314\ J\ mol^{-1}\ K^{-1} \times 298.15\ K}\right) = 2.418 \times 10^{-18}$

$Li_2S_6 \rightarrow 2LiS_3^\bullet$

$$K_{dr}^\ominus = \frac{[LiS_3^\bullet]^2}{[Li_2S_6]} = \frac{[LiS_3^\bullet]^2}{[Li_2S_6(I)] + Li_2S_6(II)]} = \frac{[LiS_3^\bullet]^2}{1.492\,[Li_2S_6(I)]} = \frac{K_{dr}^\ominus(I)}{1.492}$$

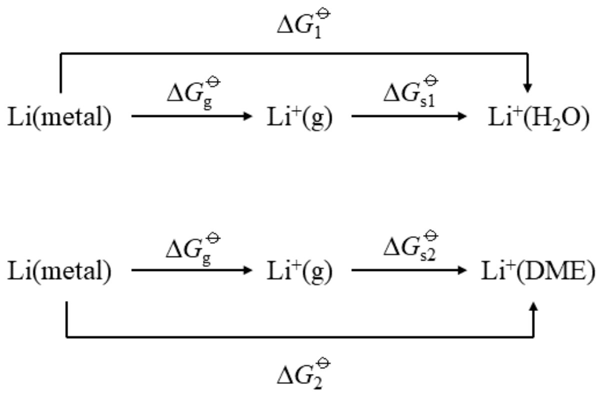
$Li_2S_6(I) \rightarrow 2LiS_3^\bullet$, $\Delta G_{dr}^\ominus(I) = -RT \ln K_{dr}^\ominus(I)$

$$K_{dr}^\ominus(I) = \exp\left(-\frac{45.13\ kJ\ mol^{-1} \times 1000}{8.314\ J\ mol^{-1}\ K^{-1} \times 298.15\ K}\right) = 1.24 \times 10^{-8}$$

$$K_{dr}^\ominus = \frac{1.24 \times 10^{-8}}{1.492} = 8.31 \times 10^{-9}$$

4 points in total
+1 point if $[Li_2S_6]$ is in the first blank, but (2),(3),(4) and $[LiS_6^-]$, $[LiS_3^\bullet]$, $[S_6^{2-}]$ are not in one-to-one correspondence.
(2), (3), (4) and $[LiS_6^-]$, $[LiS_3^\bullet]$, $[S_6^{2-}]$ must be in one-to-one correspondence, e.g. -2 points if $[LiS_3^\bullet] > [LiS_6^-] > [S_6^{2-}]$.

4.11 (6.0 pt)



$\Delta G_1^\ominus = \Delta G_\text{g}^\ominus + \Delta G_\text{s1}^\ominus \qquad (1)$ (1 point)

$\Delta G_2^\ominus = \Delta G_\text{g}^\ominus + \Delta G_\text{s2}^\ominus \qquad (2)$ (1 point)

$(2) - (1)$: $\Delta G_2^\ominus - \Delta G_1^\ominus = \Delta G_\text{s2}^\ominus - \Delta G_\text{s1}^\ominus$ (1 point)

$\text{Li(metal)} \longrightarrow \text{Li}^+(\text{H}_2\text{O}) + \text{e}^-$, $\Delta G_1^\ominus = nFE^\ominus(\text{Li}^+(\text{H}_2\text{O})/\text{Li})$ (1 point)

$\text{Li(metal)} \longrightarrow \text{Li}^+(\text{DME}) + \text{e}^-$, $\Delta G_2^\ominus = nFE^\ominus(\text{Li}^+(\text{DME})/\text{Li})$ (1 point)

$nFE^\ominus(\text{Li}^+(\text{DME})/\text{Li}) = nFE^\ominus(\text{Li}^+(\text{H}_2\text{O})/\text{Li}) - \Delta G_\text{s1}^\ominus + \Delta G_\text{s2}^\ominus$

$E^\ominus(\text{Li}^+(\text{DME})/\text{Li}) = -3.040 - \dfrac{[(-116.9\ \text{kJ mol}^{-1}) - (-114.6\ \text{kJ mol}^{-1})] \times 1000}{96485\ \text{C mol}^{-1}} = -3.016\ \text{V}$ (1 point)

6 points in total
For each calculation, consider whether the logic for solving this question is correctly established. If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.

4.12 (5.0 pt)

Assume $[S_4^{2-}] = c_1$, the original concentration of Li_2S is c_0
According to the charge balance:

$$2c_0 = 1 \times [S_3^{\bullet-}] + 2 \times [S_4^{2-}] + 2 \times [S_5^{2-}] + 2 \times [S_6^{2-}] + 2 \times [S_7^{2-}] + 2 \times [S_8^{2-}]$$ (1 point)

$$2c_0 = 17.50c_1 + 1.00 \times 2c_1 + 4.50 \times 2c_1 + 55.00 \times 2c_1 + 5.00 \times 2c_1 + 0.75 \times 2c_1 = 150c_1$$

$$c_0 = 75c_1$$ (1point)

According to the material balance:

$$c_0 + \frac{4.81\ \text{mg}}{32.07\ \text{g mol}^{-1} \times 10.00\ \text{mL}}$$

$$= 17.50 \times 3c_1 + 1.00 \times 4c_1 + 4.50 \times 5c_1 + 55.00 \times 6c_1 + 5.00 \times 7c_1 + 0.75 \times 8c_1$$ (1 point)

$$75c_1 + 0.0150\ \text{mmol mL}^{-1} = 450c_1$$ (1 point)

$$c_1 = 4.00 \times 10^{-5}\ \text{mmol mL}^{-1}$$

$$m(Li_2S) = 75 \times 4.00 \times 10^{-5}\ \text{mmol mL}^{-1} \times 10.00\ \text{mL} \times 45.96\ \text{g mol}^{-1} = 1.38\ \text{mg}$$ (1 point)

5 points in total
For each calculation, consider whether the logic for solving this question is correctly established.
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.

[Marking Scheme] Interconversion among Nitrogen Oxides

15% of the total											
Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	5.10	**Total**
Points	4	4	2	4	3	8	4	6	4	6	**45**
Score											

5.1 (4.0 pt)

Using the definition of $K_{c1} = \frac{[N_2O_2]}{[NO]^2}$, $[N_2O_2] = K_{c1}[NO]^2$ is obtained.

Thus, $r_+ = k_2[N_2O_2][O_2] = k_2K_{c1}[NO]^2[O_2]$

4 points in total
1 point for the correct expression of K_{c1}
1 point for the expression of r_+ with $[N_2O_2]$ and $[O_2]$
1 point for the correct $[N_2O_2]$
1 point for the correct r_+

5.2 (4.0 pt)

Combining $K_{c1} = \exp(M - N/T)$, $k_2 = A_2 \exp\left(-\frac{E_{a,2}}{RT}\right)$ and $k_+ = k_2K_{c1}$,

$k_+ = k_2K_{c1} = A_2 \exp\left(-\frac{E_{a,2}}{RT}\right) \exp\left(M - \frac{NR}{RT}\right) = A_2 \exp(M) \exp\left(-\frac{E_{a,2} + NR}{RT}\right)$.

Comparing this equation with Arrhenius equation,
$A_+ = A_2 \exp(M)$ and $E_{a+} = E_{a,2} + NR$ are obtained.

4 points in total
1 point for the correct expression of k_2
1 point for the correct expression of k_+ with $E_{a,2}$, A_2, M and N
1 point for the correct expression of A_+
1 point for the correct expression of E_{a+}

5.3 (2.0 pt)

Calculation:

According to Arrhenius equation, $\ln\frac{k_+(T_2)}{k_+(T_1)} = \frac{E_{a+}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ is obtained.

Thus, $k_+(700\ \text{K}) = 6.86 \times 10^5\ \text{L}^2\ \text{mol}^{-2}\ \text{min}^{-1}$

2 points in total
If $k_+(700\ \text{K})$ is incorrect due to miscalculation, 1 point will be deducted.

5.4 (4.0 pt)
Calculation:
Because $\Delta_r H_m^\ominus$ and $\Delta_r S_m^\ominus$ do not change with temperature,
$\Delta_r H_m^\ominus(600K)$
$= \Delta_r H_m^\ominus(298K)$
$= 2\Delta_f H_m^\ominus(NO_2, 298K) - \Delta_f H_m^\ominus(NO, 298K) - \Delta_r H_m^\ominus(O_2, 298K)$
$= -116.4$ kJ mol^{-1}

$\Delta_r S_m^\ominus(600K)$
$= \Delta_r S_m^\ominus(298K)$
$= 2S_m^\ominus(NO_2, 298K) - 2S_m^\ominus(NO, 298K) - S_m^\ominus(O_2, 298K)$

-146.6 J K^{-1} mol^{-1}
For a thermostatic process, $\Delta G = \Delta H - T\Delta S$, thus $\Delta_r G_m^\ominus(600\text{ K}) = -28.44$ kJ mol^{-1}
Using the equation of $K_p^\ominus = \exp(-\Delta_r G_m^\ominus / RT)$, $K_p^\ominus(600\text{ K}) = 299.2$ is obtained.

4 points in total
1 point for the correct value of $\Delta_r H_m^\ominus(600\text{ K})$
1 point for the correct value of $\Delta_r S_m^\ominus(600\text{ K})$
1 point for the correct value of $\Delta_r G_m^\ominus(600\text{ K})$ or the correct relationship among $\Delta_r H_m^\ominus(600\text{ K})$, $\Delta_r S_m^\ominus(600\text{ K})$ and $K_p^\ominus(600\text{ K})$
1 point for the correct value of $K_p^\ominus(600\text{ K})$
If any miscalculation exists, 1 point will be deducted.

5.5 (3.0 pt)
Calculation:
Using the equation of $\Delta_r U_m^\ominus = \Delta_r H_m^\ominus - \sum \nu RT$ and $\sum \nu$ value of -1 ($\nu_{NO_2} - \nu_{NO} - \nu_{O_2} = 2 - 2 - 1 = -1$), $\Delta_r U_m^\ominus(600\text{ K}) = -111.4$ kJ mol^{-1} is obtained.

3 points in total
1 point for the correct relationship between $\Delta_r U_m^\ominus$ and $\Delta_r H_m^\ominus$
1 point for the correct value of $\Sigma\nu$
1 point for the correct value of $\Delta_r U_m^\ominus(600\text{ K})$
If $\Delta_r U_m^\ominus(600\text{ K})$ is incorrect due to miscalculation, 0.5 points will be deducted

5.6 (6.0 pt)
Calculation:

When chemical equilibrium is reached, $K_c = \frac{[\mathrm{NO_2}]_{\mathrm{eq}}^2}{[\mathrm{NO}]_{\mathrm{eq}}^2 [\mathrm{O_2}]_{\mathrm{eq}}}$ and $r_{-\mathrm{eq}} = r_{+\mathrm{eq}}$.

Thus, $r_{-\mathrm{eq}} = r_{+\mathrm{eq}} = k_+ [\mathrm{NO}]_{\mathrm{eq}}^2 [\mathrm{O_2}]_{\mathrm{eq}} = k_+ \frac{[\mathrm{NO_2}]_{\mathrm{eq}}^2}{K_c} = k_- [\mathrm{NO_2}]_{\mathrm{eq}}^2$

Therefore, $r_- = k_- [\mathrm{NO_2}]^2$

Using the equation of $K_c = K_p^{\ominus} \left(\frac{RT}{p^{\ominus}}\right)^{-\sum_{\mathrm{B}} \nu_{\mathrm{B}}}$ and $K_p^{\ominus}$ (600 K) value of 299.2, $K_c = 1.49 \times 10^4$ L mol^{-1} is obtained.

According to $k_- = k_+ / K_c$, the value of k_- is calculated to be 44.4 L mol^{-1} min^{-1} If the $K_p^{\ominus}$(600 K) value is used as 350.0, the result should be 38.0.

8 points in total
1 point for the consideration of $r_{-\mathrm{eq}} = r_{+\mathrm{eq}}$
2 points for the correct expression of r_-
1 point for the correct relationship among k_+, K and k_-
4 points for the correct value of k_-
If $K_p^{\ominus}$ instead of K_c is used, 2 points will be deducted
If k_- is incorrect due to miscalculation, 1 point will be deducted

5.7 (4.0 pt)
Calculation:
According to the stoichiometry of the reaction and setting $p_{\mathrm{NO_2}} = 0.8p_0, p_{\mathrm{NO}} = 0.2p_0$ and $p_{\mathrm{O_2}} = 0.1p_0$ are obtained.

$$K_p^{\ominus} = \frac{\left(p_{\mathrm{NO_2}}/p^{\ominus}\right)^2}{\left(p_{\mathrm{NO}}/p^{\ominus}\right)^2 \left(p_{\mathrm{O_2}}/p^{\ominus}\right)} = \frac{(0.8p_0/p^{\ominus})^2}{(0.2p_0/p^{\ominus})^2 (0.1p_0/p^{\ominus})} = \frac{160p^{\ominus}}{p_0}$$

Therefore, $p_0 = 53.5$ kPa. $p_{\mathrm{total}} = p_{\mathrm{NO_2}} + p_{\mathrm{NO}} + p_{\mathrm{O_2}} = 1.1p_0 = 58.8$ kPa
If the $K_p^{\ominus}$(600 K) value is used as 350.0, the result of 50.3 kPa is obtained.

4 points in total
1 point for the expression of $K_p^{\ominus}$. If $p^{\ominus}$ is omitted, no penalty.
1 point for the correct ratio among $p_{\mathrm{NO_2}}$, p_{NO} and $p_{\mathrm{O_2}}$
2 points for the correct value of p_{total}
If p_{total} is incorrect due to miscalculation, 1 point will be deducted

5.8 (6.0 pt)
The given mechanism involves a pre-equilibrium:
$r_{S+1} = r_{S-1}, k_{S+1}[O_2]\theta_v^2 = k_{S-1}\theta_O^2, \theta_O/\theta_v = (k_{S+1}[O_2]/k_{S-1})^{0.5}$
$r_{S+2} = r_{S-2}, k_{S+2}[NO]\theta_v = k_{S-2}\theta_{NO}, \theta_{NO}/\theta_v = k_{S+2}[NO]/k_{S-2}$
$r_{S+4} = r_{S-4}, k_{S+4}\theta_{NO_2} = k_{S-4}[NO_2]\theta_v, \theta_{NO_2}/\theta_v = k_{S-4}[NO_2]/k_{S+4}$
Because $\theta_v + \theta_{NO} + \theta_{NO_2} + \theta_O = 1$, using the ratios among these coverages,
$\theta_v = \dfrac{1}{1 + (k_{S+1}[O_2]/k_{S-1})^{0.5} + k_{S+2}[NO]/k_{S-2} + k_{S-4}[NO_2]/k_{S+4}}$ is obtained.

6 points in total
1 point for the correct expression of θ_0/θ_v
1 point for the correct expression of θ_{NO}/θ_v
1 point for the correct expression of θ_{NO2}/θ_v
1 point for the utilization of the normalized condition
2 points for the correct expression of θ_v
If no derivation is provided, 6 points for the correct expression of θ_v
One of the numerator and the four parts of the denominator of this expression is wrong, 4 points; two of them are wrong, 2 points; three or more are wrong, 0 point.

5.9 (4.0 pt)

(B)

4 points for choosing (B)
2 points for choosing (A)
0 points for other choices

5.10 (6.0 pt)

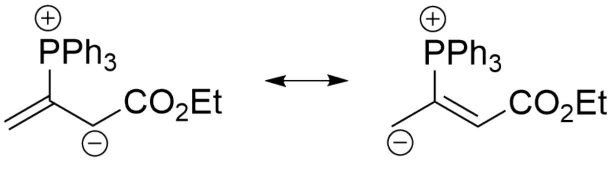
(B)

6 points for choosing (B)
0 points for other choices

[Marking Scheme] Enabling Phosphines

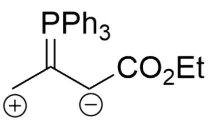
6.1 (3.0 pt)
R
3 points in total;
3 points for assigning as *R*

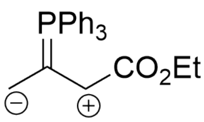
6.2 (6.0 pt)

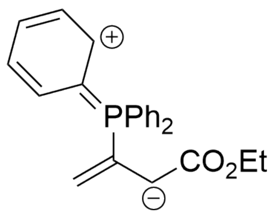


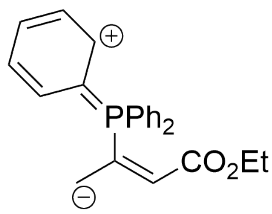
A **A'**

6 points in total.
3 points for each;
no points if any structure containing C=P is given:

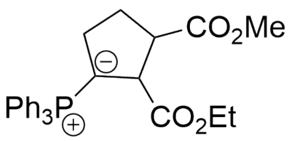




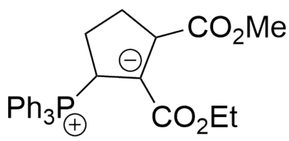




6.3 (8.0 pt)



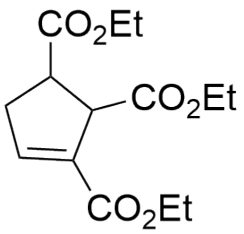
B'



C'

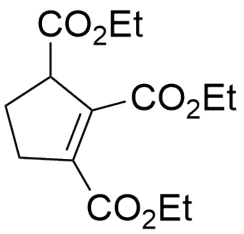
8 points in total.
4 points for each.
Reasonable resonance structures of **B'** and **C'** are also acceptable.
1 point is given if structures with two methyl esters or two ethyl esters.

6.4 (5.0 pt)

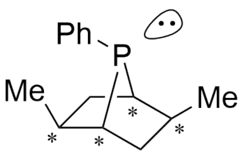


6

5 points in total.
2 points if the isomerized structure is given:



6.5 (6.0 pt)



P2

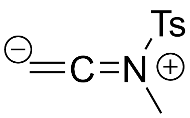
6 points in total.
6 points for 4 correct asterisks, 1.5 points for each;
−1.5 points for every wrong asterisk till 0 points.

6.6 (3.0 pt)
90:10
3 points in total;
3 points for the correct answer: 90/10 or 9/1 or 9

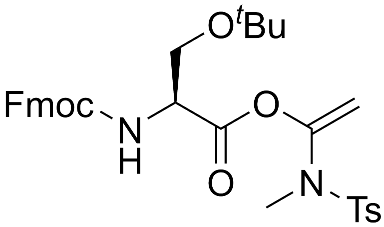
6.7 (5.0 pt)
(d)
5 points in total;
5 points for choosing (d)

Organic Molecules in Life

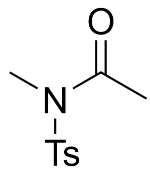
7.1 (12.0 pt)



7

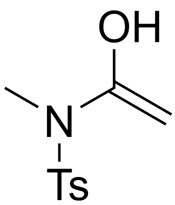


9

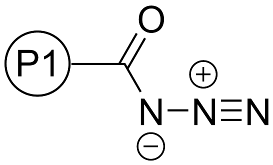


12

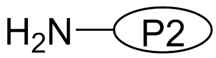
12 points in total.
4 points for each;
2 points for the enantiomer of **9**, or the structure missing the chirality is given;
2 points if the enol form of **12** is given:



7.2 (8.0 pt)

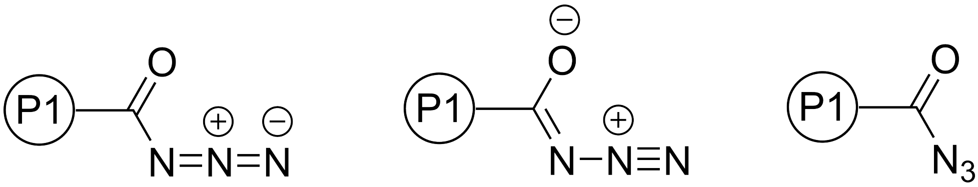


15

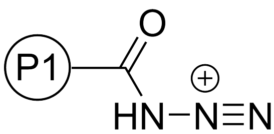


16

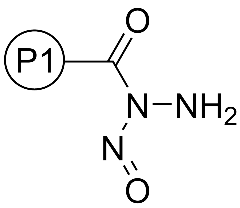
8 points in total.
4 points for each;
4 points for the resonance structures of **15** or if azide is written as N_3:



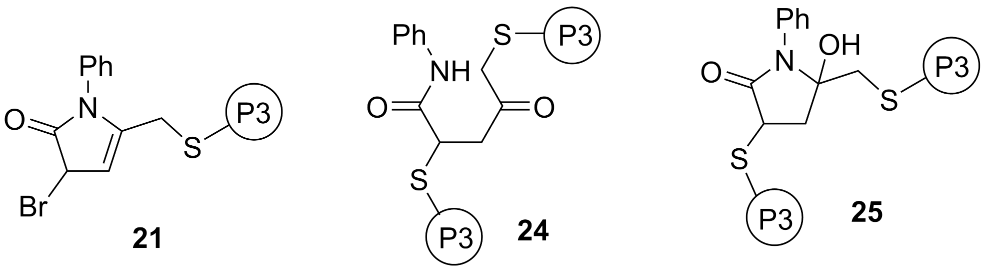
2 points for its protonated form:



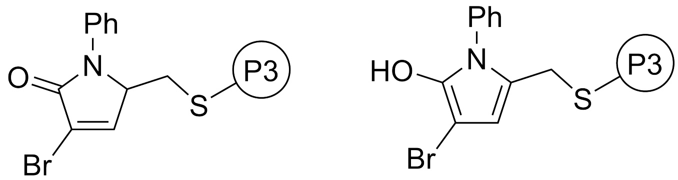
1 point if the nitrosonation on the nitrogen linked to carbonyl is given:



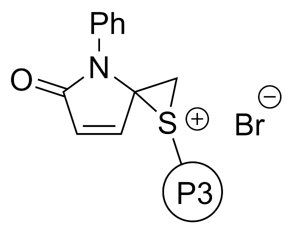
7.3 (12.0 pt)



12 points in total.
4 points for the isomers of **21**:



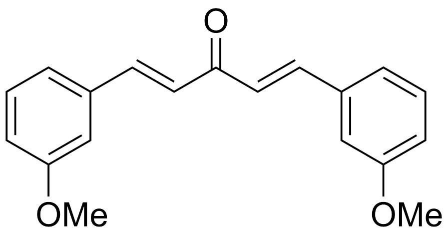
2 points if the form of NGP is given:



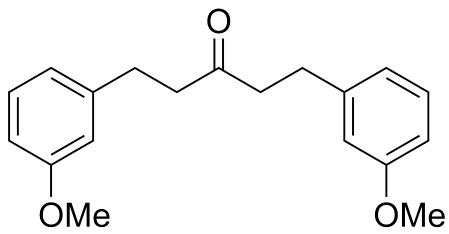
1 point if the second protein is added at the β position of amide group, and no double punishment for **24** and **25**.

[Marking Scheme] Amazing Chiral Spiro Catalyst

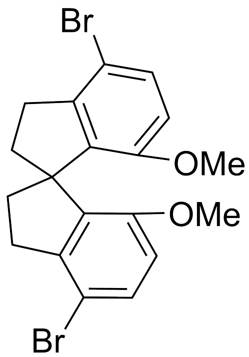
8.1 (16.0 pt)



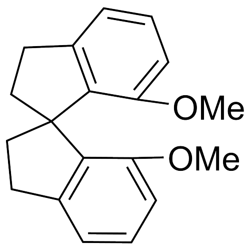
1



2



4



5

16 points in total.
4 points for each correct structure as shown above.
4 points if the *cis* isomer of **1** is given
2 points if the regioisomer of **4** is given

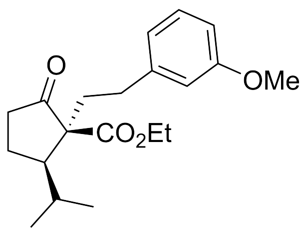
8.2 (2.0 pt)
(c)
2 points in total;
2 points for choosing (c)

8.3 (2.0 pt)
(b)
2 points in total;
2 points for choosing (b)

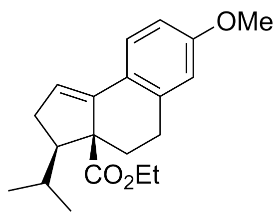
8.4 (2.0 pt)
Ir(III) or +3
2 points in total;
2 points for Ir(III) or +3

8.5 (2.0 pt)
6
2 points in total;
2 points for 6

8.6 (8.0 pt)



15



16

8 points in total.
4 points for each;
2 points for correct skeleton, missing or wrong stereochemistry;
2 points if the regioisomer of **16** is given

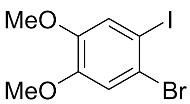
8.7 (2.0 pt)
(b)
2 points in total;
2 points for choosing (b)

8.8 (2.0 pt)
(a)
2 points in total;
2 points for choosing (a)

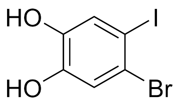
[Marking Scheme] Total Synthesis of Capitulactone

9% of the total					
Question	9.1	9.2	9.3	9.4	**Total**
Points	24	2	16	2	**44**
Score					

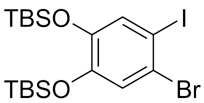
9.1 (24.0 pt)



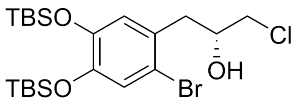
3



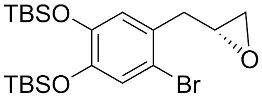
4



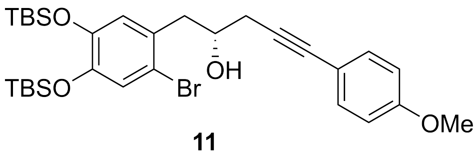
5



8



9

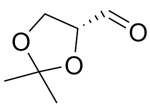


11

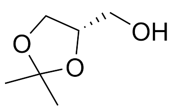
24 points in total.
4 points for each;
2 points for each structure of **8**, **9** or **11** with missing or wrong stereochemistry.

9.2 (2.0 pt)
(d)
2 points in total;
2 points for choosing (d)

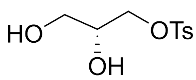
9.3 (16.0 pt)



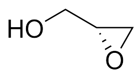
15



16



18



19

16 points in total.
4 points for each;
2 points if structure with missing or wrong stereochemistry is given.

9.4 (2.0 pt)
(b)
2 points in total;
2 points for choosing (b)