

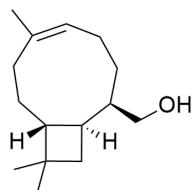
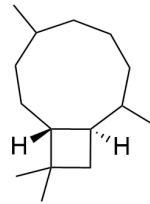
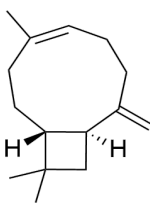


## 1. Isocaryophyllene, clovene, and humulene

6% of total

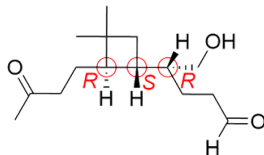
1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	Total
7	3	6	2	2	8	2	2	2	34

1.1 (7 pt)

<p><b>A (2 pt)</b></p>  <p><i>The trans-isomer gets full marks.</i></p> <p>-1 pt if missing a carbon atom in the ring/ added another carbon atom in the ring.</p>	<p><b>B (2 pt)</b></p>  <p>Also 2 pt if the structure is incorrect, but consistent with isocaryophyllene (and 2 equivalents of H<sub>2</sub> are added).</p>
<p><b>Iso-caryophyllene (i-Cy) (3 pt)</b></p>  <p>-1 pt if missing a carbon atom/ added another carbon atom in the ring.</p> <p>-1 pt If a ring is made by combining two other C atoms and added a methyl to the other carbon.</p> <p>-2 pt if no second ring is present; only added CH<sub>3</sub> to all/one/two carbonyls in the right-hand structure.</p> <p><i>The trans-isomer gets full marks. Stereochemistry will not be marked for A, B or i-Cy.</i></p>	



1.2 (3 pt)



Each centre correctly circled ½ pt.

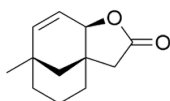
Each descriptor correct ½ pt.

If incorrect centre is circled then -1pt per incorrect circle.

Minimum score is 0pt

1.3 (6 pt)

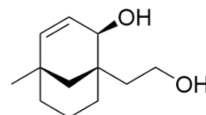
E (3 pt)



-2 pt if the structure is not cyclic and only the ester is removed.

Stereochemistry will not be marked.

F (3 pt)



-2 pt for reducing the ester to an aldehyde (and alcohol).

Stereochemistry will not be marked.

1.4 (2 pt)

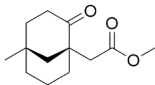
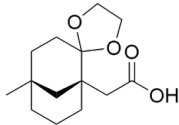
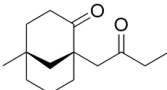
- ☐ PCC
  - ☐ K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O
  - ☒ MnO<sub>2</sub>
  - ☐ (i) OsO<sub>4</sub>, (ii) KHSO<sub>3</sub>
- 0 pt if any other box(es) ticked.

1.5 (2 pt)

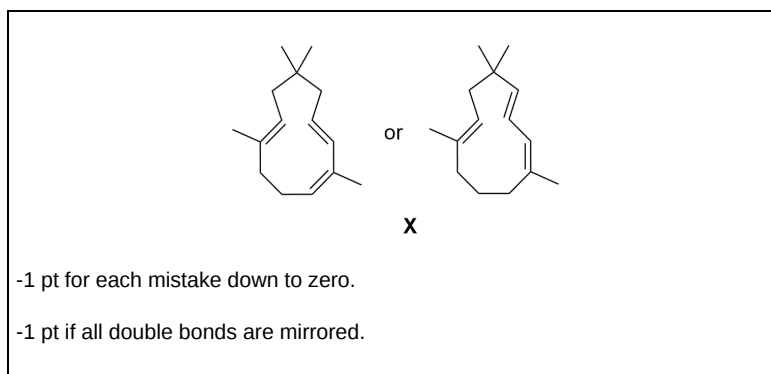
- ☐ PCC
  - ☒ K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O
  - ☐ MnO<sub>2</sub>
  - ☐ (i) OsO<sub>4</sub>, (ii) KHSO<sub>3</sub>
- 0 pt if any other box(es) ticked.



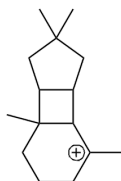
1.6 (8 pt)

<p><b>I (3 pt)</b></p>  <p>-2 pt if double bond is not reduced. -1 pt if ester is not formed. (minimum score is 0 pt)</p>	<p><b>J (2 pt)</b></p>  <p>-1 pt if acetal group is incorrect/not present. -1 pt if original ester is still present; protective group is in place. -1.5 pt if ester is formed with ethylene glycol.</p>
<p><b>K (3 pt)</b></p>  <p>-1 pt if acetal protecting group is still present. -2 pt if acid is turned into acid chloride and protective group is removed. -2 pt if five-membered ring is already formed with an alcohol group still present.</p>	

1.7 (2 pt)



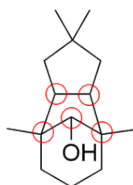
1.8 (2 pt)



**Y**

0 pt if any other charge/group has been added to the structure.

1.9 (2 pt)



2 pt if five circles are correct.

1 pt if four circles are correct and one incorrect/missing.

0 pt for more than five carbons circled or two or more incorrect/missing.



## 2. Rapamycin - A molecular glue

6.5% of the total

2.1	2.2	2.3	2.4	Total
12	19	18	18	67

### 2.1a

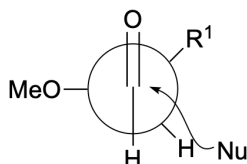
Correct 8 pts

-2 pts if nucleophile approach not shown or incorrect

4 pts if chirality at rear carbon is wrong, but MeO placed perpendicular

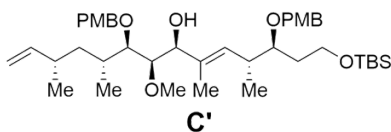
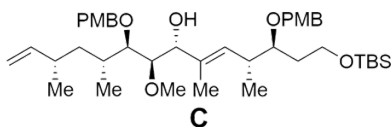
4 pts if chirality at rear carbon is correct, but MeO not placed perpendicular

Need to use Felkin-Anh model without chelation and put electronegative group OMe perpendicular to aldehyde.



### 2.1b

Structure of **C** fully correct 4 pts. If **C'** is given 2 pts.



If partly correct:

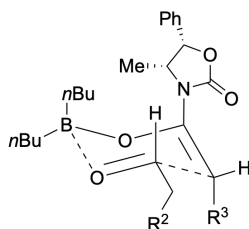
Absolute stereochemistry of OH and OMe is correct 2 pts. If incorrect, but the relative stereochemistry is correct 1 pt.

-1 pt for each error in each molecule in functional groups not undergoing reaction.

No error carried forward awarded even if part a is incorrect as stereochemistry can be inferred from the final structure of rapamycin



Six-membered ring Zimmerman-Traxler Model:

CN1C(=O)O[C@H](C1)c2ccccc2

**X**

—H

Chemical structure of a cyclohexane ring with a wavy line, a methoxy group (OMe), and a tert-butyldimethylsilyl ether group (OTBS).

$$R^2 \text{---} \text{---} \text{---}$$

—H

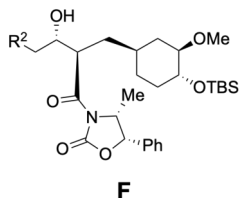
-1 pt for each trivial mistake



2.2b

Structure of **F** (with stereochemistry) 4 pts

-1 pt for each error of functional groups not undergoing reaction (trivial error).



No error carried forward awarded even if part **2.2a** is incorrect as stereochemistry can be inferred from the final structure of rapamycin.

If partly correct:

Absolute stereochemistry of newly formed stereocenters is correct 2 pts. If incorrect, but the relative stereochemistry is correct 1 pt.

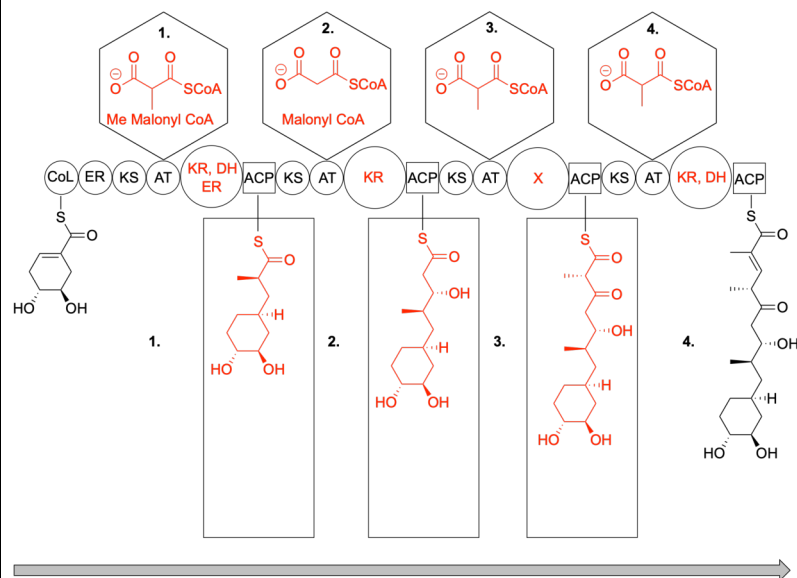
-1 pt for each error in each molecule in functional groups not undergoing reaction.



### 2.3

Hexagons for building blocks are worth 1 pt each. Total = 4 pts  
Circles for enzymes and rectangles for structures worth 2 pts each. Total 14 pts.  
No partial credit for this part. The order of the enzymes in the circles is not graded.

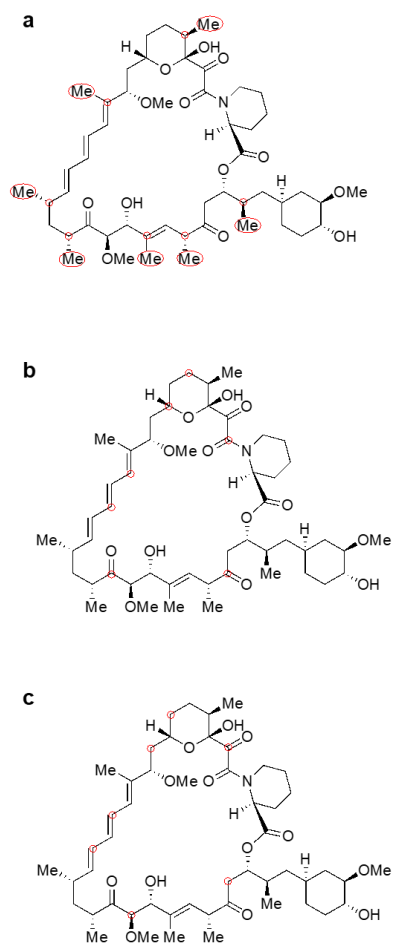
Error carried forward can be implemented for the structures in the rectangles.







2.4





Each of the three parts is worth 6 pts. The number of “accurate circles” = number of correct circles – number of incorrect circles.

If the **b** and **c** are swapped and both perfectly correct: 6 pts are awarded for **b + c**.

In all other cases they will be marked as **b** and **c** as indicated.

#### 2.4a

14 accurate circles = 6 pts  
12-13 accurate circles = 5 pts  
10-11 accurate circles = 4 pts  
8-9 accurate circles = 3 pts  
6-7 accurate circles = 2 pts  
4-5 accurate circles = 1 pt  
< 4 accurate circles = 0 pt

#### 2.4b

7 accurate circles = 6 pts  
6 accurate circles = 5 pts  
5 accurate circles = 4 pts  
4 accurate circles = 3 pts  
3 accurate circles = 2 pts  
2 accurate circles = 1 pt  
< 2 accurate circles = 0 pts

#### 2.4c

7 accurate circles = 6 pts  
6 accurate circles = 5 pts  
5 accurate circles = 4 pts  
4 accurate circles = 3 pts  
3 accurate circles = 2 pts  
2 accurate circles = 1 pt  
< 2 accurate circles = 0 pts



### 3. Lanterns and the Burj Khalifa

7.5% of the total

3.1	3.2	3.3	3.4	3.5	3.6	3.7	Total
6	4	4	5	40	20	32	111

3.1

Angle	A	B	C
0°			✓
30°			
45°			
60°			
90°			
120°		✓	
135°			
180°	✓		

6 pt (2 pt each). No pts if more than one angle ticked for any ligand.

3.2

$F < D < E$
4 pt
2 pt if it is in the opposite order: $(E < D < F)$

3.3

$Q$	2
$(h, k)$	(1, 1)
$V$	12
$E$	24
$F$	14
$F_3$	8
$F_4$	6

4 pt (1 pt each). No credit if numbers placed in wrong rows.

3.4

$Q$	4
$(h, k)$	(0, 2) or (2, 0)
$V$	24
$E$	48
$F$	26
$F_3$	8
$F_4$	18

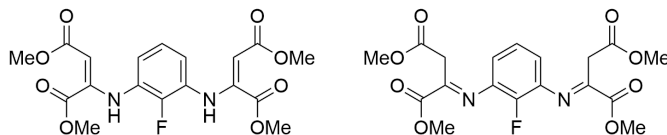
5 pt. (1 pt each). No credit if numbers placed in wrong rows.



### 3.5

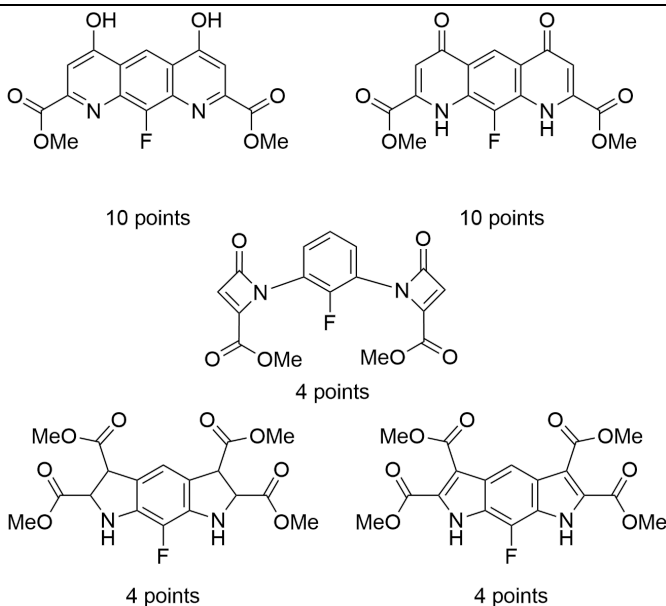
Please note that although there are lots of points per structure in this part, this is to balance the weighting with the rest of the question. There will generally be a penalisation of **-2 pt** per trivial error in this part.

#### H



**8 pt.** Stereochemistry is not required. Alkenes can be drawn as *cis* or *trans*. Imine tautomer scores full credit. Structures without the correct formulae score zero; except for trivial mistakes. These will give a maximum of **6 pt**.

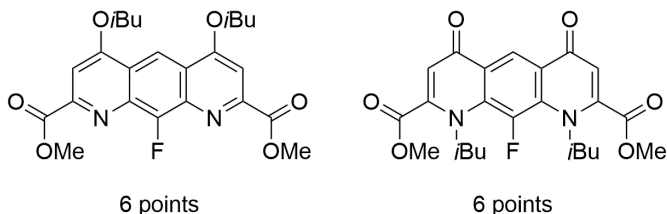
#### I



**10 pt.** Pyridone tautomer **10 pt** Four-membered ring lactam (matches formula but strained) **4 pt.** Indole/indolene structure **4 pt.** Error carried forward from **H** can be given, but maximum **6 pt** for structures that do not match formula.

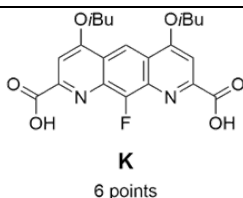


J



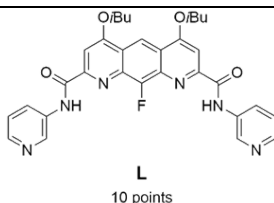
**6 pt.** Error carried forward from **I** can be given as follows. All sufficiently acidic OH and NH groups on structure have undergone correct Mitsunobu alkylation **6 pt.** Some but not all sufficiently acidic OH and NH groups have undergone alkylation **4 pt.** Student has alkylated OH or NH groups which would be unreactive (standard alcohol OH or amine NH) **4 pt.** *OtBu* or *NiBu* groups in product, but corresponding starting material was not OH/NH **2 pt.** Further penalty of **-1 pt** if *iPr* drawn instead of *iBu*.

K



**6 pt.** Error carried forward from **J** can be given, but structure must have undergone correct ester hydrolysis reaction. For error carried forward other base labile functional groups must be hydrolysed.

L



**10 pt.** Error carried forward from **K** can be given, but structure must have undergone feasible reaction under these conditions for full credit. All structures (including any error carried forward) will be penalised as follows: **-2 pt** if ligand does not have two planes of symmetry, **-2 pt** for not 180° angle with both outer rigid pieces, **-2 pt** for not 120° angle with central rigid piece, **-2 pt** if carbons from oxalyl chloride have been incorporated.



3.6

	C	C	C	C
	C	C	C	C
	A	C	A	C
	A	C	A	A

**20 pt.** There is a 50% chance of guessing each box correctly and so these are not individually marked. Firstly the number of accurate boxes (x) is calculated from the number of correct boxes minus the number of incorrect boxes. The total number of pt (y) is calculated from the number of accurate boxes (x) using this relationship:


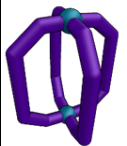
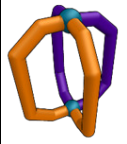
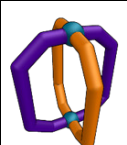
$$y = \frac{20}{1 + e^{-0.5(x-8)}}$$



Accurate boxes	Pt
0	0.00
1	0.59
2	0.95
3	1.52
4	2.38
5	3.65
6	5.38
7	7.55
8	10.00
9	12.45
10	14.62
11	16.35
12	17.62
13	18.48
14	19.05
15	19.41
16	20.00



3.7

				
	2 (1 pt)	2	2 (1 pt)	2 (1 pt)
	2 (2 pt)	8 (4 pt)	4	2 (2 pt)
	1 (2 pt)	4 (4 pt)	3 (4 pt)	2 (2 pt)
	1 (2 pt)	2 (2 pt)	1 (2 pt)	1 (3 pt)

32 pt

No partial credit for any other answer in a box. No credit for alternative version where columns or rows have been swapped etc. No error carried forward from previous question.





أولمبياد الكيمياء الدولي السابع والخمسون  
الإمارات العربية المتحدة  
57<sup>th</sup> IChO - United Arab Emirates - 2025

The isomers are drawn out below (this is not needed from students and is included just as information for mentors).

	 Code: 1111 Code: 3333	 Code: 1112 Code: 3334	 Code: 1122 Code: 3344	 Code: 1212 Code: 3434
	 Code: 1113 Code: 1333	 Code: 1114 Code: 1444  Code: 1123 Code: 1433 Code: 1142 Code: 1344  Code: 1132 Code: 1334 Code: 1124 Code: 1443  Code: 1213 Code: 1343		 Code: 1214 Code: 1434
	 Code: 1133	 Code: 1134 Code: 1332  Code: 1143 Code: 1233	 Code: 1144 Code: 1342  Code: 1243	 Code: 1234 Code: 1432
	 Code: 1313	 Code: 1314 Code: 1323	 Code: 1324	 Code: 1414



## 4. The life of tennis balls

6% of the total

4.1	4.2	4.3	4.4	Total
3	16	5	16	40

### 4.1

The inner ball pressure is equal to the atmospheric pressure.  
The average molar mass of air,

$$M = 0.8 \times 28.02 \text{ g mol}^{-1} + 0.2 \times 32.00 \text{ g mol}^{-1} = 28.816 \text{ g mol}^{-1}$$

1 pt

The ball volume is:

$$V = \frac{4}{3}\pi R^3 = \frac{4}{3} \cdot \pi \cdot (3.0)^3 = 113.1 \text{ mL}$$

1 pt

Using the ideal gas law, we find the air mass as follows:

$$p = \frac{nRT}{V} = \frac{mRT}{MV} \Rightarrow m = \frac{pMV}{RT} = \frac{101325 \text{ Pa} \times 28.816 \text{ g mol}^{-1} \times 1.131 \times 10^{-4} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} = 0.133 \text{ g}$$

1 pt

### 4.2

We can find the quantity of gas C:

$$n = \frac{pV}{RT} = \frac{(161975 - 101325) \text{ Pa} \times \frac{4}{3}\pi \cdot (0.03 \text{ m})^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$
$$= 2.767 \times 10^{-3} \text{ mol} \quad \text{1 pt}$$

The reaction with HI indicates a possible redox reaction with formation of  $\text{I}_2$  (which is confirmed by the positive result in the further reaction with  $\text{Na}_2\text{S}_2\text{O}_3$ ).

Thus, **A** or **B** is an oxidant. If  $\text{Ag}^+$  is added to **A+B** there is the formation of precipitate(s) (likely containing  $\text{Ag(I)}$ ) but we don't know if it is one or several compounds. We note that **reaction 2** gives approximately half the amount of precipitate as the final reaction. This could mean that the precipitate from the final reaction is a mixture of two precipitates, one of which is not formed in **reaction 2**.

We might first guess an equimolar amount of each precipitate from **reaction 2** and that the number of moles of each precipitate is the same the number of moles of gas C, ( $2.767 \times 10^{-3} \text{ mol}$ ).

If this is the case, we can calculate a molar mass for the precipitate:

$$M = \frac{0.4112 \text{ g}}{2.767 \times 10^{-3} \text{ mol}} = 148.61 \text{ g mol}^{-1}$$

Assuming the cation is  $\text{Ag(I)}$  ( $= 107.87 \text{ g mol}^{-1}$ ), this leaves an anion of  $40.74 \text{ g mol}^{-1}$ . 1 pt

Remembering that this mass was only approximate, this is consistent with the anionic part being a chloride ion ( $= 35.45 \text{ g mol}^{-1}$ ) and the precipitate being  $\text{AgCl}$ . Upon addition of excess chloride,  $\text{AgCl}$  redissolves and thus this is consistent with **B** containing



chloride ions. **2 pt**

Indeed, there is several qualitative indications that the precipitate could be AgCl.

Now we know accurately the molar mass of the first precipitate, we can calculate the accurate molar mass of the second precipitate (= 153.90 g mol<sup>-1</sup>). Assuming the cation is Ag(I), the anionic part has a molar mass of 46.03 g mol<sup>-1</sup>. **2 pt**

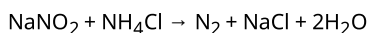
There are no single atoms that fit this charge and mass combination. If we consider atoms of common elements then we can deduce the anion is nitrite (46.01 g mol<sup>-1</sup>) and the precipitate as AgNO<sub>2</sub>. **2 pt**

Hence, **A** is a nitrite salt and **B** is a chloride salt. Again, taking equimolar ratios as a first guess, we can calculate the sum of the cation molar masses in **A+B**. (122.48 - 35.45 - 46.01) g mol<sup>-1</sup> = 41.02 g mol<sup>-1</sup>. **1 pt**

As we know **A** is an oxidant due to the nitrite, **reaction 1** is likely a redox reaction.

However, it is the cation in **B** that is likely oxidised (as oxidation of chloride is difficult). One possibility would be the ammonium cation, and this also has a low molar mass. **2 pt**

The remaining molar mass (41.02 - (14.01+4x1.008)) g mol<sup>-1</sup> = 22.98 g mol<sup>-1</sup> is consistent with the second cation being Na<sup>+</sup>, so this is a possible answer. **1 pt**



We then conclude that **C** would be N<sub>2</sub>. **2 pt**

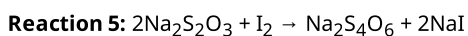
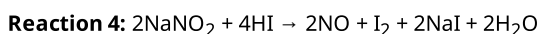
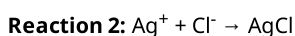
If nitrite acts as an oxidant in **reaction 4**, then gas **D** has contains a nitrogen atom in an oxidation state of lower than +3. Examples include NO, N<sub>2</sub>O or NH<sub>3</sub>, but only NO has a density similar to N<sub>2</sub>. **2 pt**

The **reaction 3** helps us understand that compound **B** is amonium salt: NH<sub>4</sub>Cl thus **A** is NaNO<sub>2</sub>

<b>A:</b> NaNO <sub>2</sub>	<b>B:</b> NH <sub>4</sub> Cl	<b>C:</b> N <sub>2</sub>	<b>D:</b> NO
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**Total 16 pts.** All **16 pts** will be given if the boxes above are all correct.

#### 4.3



**1 pt** each reaction equation = **5 pt total**, **-0.5 pt** if not balanced correctly.



#### 4.4a

Atmospheric pressure and therefore the final pressure is 1.00 atm. The pressure above atmospheric is therefore 0.80 atm initially, 0.40 atm after 241 h, and 0.19 atm after  $t_2 = 21$  days (i.e. 504 hours). We remind that  $t_2$  is approximate and using it we obtain an approximate data.

For the kinetics of the first order we have next equation:

$$\ln \frac{P_0}{P_t} = kt$$

Thus we could write two equation to find dressurisation rate constant for  $N_2$ .

$$\ln \frac{0.8}{0.4} = k_{N_2} \cdot 241 \Rightarrow k_{N_2} = \frac{1}{241} \cdot \ln \frac{0.8}{0.4} = 2.88 \cdot 10^{-3} h^{-1} \quad \ln \frac{0.8}{0.19} = k_{N_2} \cdot 21 \cdot 24 \Rightarrow k_{N_2} = \frac{1}{504} \cdot \ln \frac{0.8}{0.19} = 2.85 \cdot 10^{-3} h^{-1}$$

**1.5 pt for each equation = 3pt**

The rate constants are very close, thus the kinetics process is of the first order.

Knowing that  $t_2$  was approximate for the final version we use

$$k_{N_2} = 2.88 \cdot 10^{-3} h^{-1}$$

**1 pt (-0.5 pt  $k_{N_2} = 2.85 \cdot 10^{-3} h^{-1}$  or average of both constants)**

#### 4.4b

Next, we write equations for the initial processes for the  $N_2$  ball ( $v_{N_2}$ ) and air ball ( $v_{air}$ ) considering partial pressures and the initial difference of pressure  $\Delta P_0$ :

$$v_{0 N_2} = k_{N_2} \Delta P_0 \quad \mathbf{1 \text{ pt } (-0.25 \text{ pt if the absolute pressure } P_0 \text{ is considered)}}$$

$$v_{0 air} = k_{N_2} \cdot 0.8 \Delta P_0 + k_{O_2} \cdot 0.2 \Delta P_0 \quad \mathbf{1 \text{ pt } (-0.25 \text{ pt if the absolute pressure considered)}}$$

As we know that the second process is 10% faster than the first, we can find  $k_{O_2}$ :

$$\frac{v_{0 air}}{v_{0 N_2}} = \frac{0.8 k_{N_2} \Delta P_0 + 0.2 k_{O_2} \Delta P_0}{k_{N_2} \Delta P_0} = \frac{1.10}{1.00} \quad \mathbf{1 \text{ pt}}$$

$$0.3 \cdot k_{N_2} = 0.2 \cdot k_{O_2} \quad \mathbf{1 \text{ pt}}$$

$$k_{O_2} = 1.5 \cdot k_{N_2} = 4.31 \times 10^{-3} h^{-1} \quad \mathbf{1 \text{ pt}}$$

or for  $k_{O_2} = 1.5 \times 10^{-3} h^{-1}$  the given value of  $k_{N_2} = 1.0 \times 10^{-3} h^{-1}$



#### 4.4c

We need to consider the following factors:

- (a) The initial inner ball pressure varies with the temperature (**1 pt**);
- (b) The final pressure is the same (1 atm) and taken into account (**2 pts**);
- (c) The rate constant varies with the temperature via Arrhenius equation (**2 pts**).

So next equations should be considered

(a) The initial pressure,  $p_{0(T)}$ , at another temperature,  $T$ , is  $p_{0(T)} = p_{0(298.15)} \cdot \frac{T}{298.15 \text{ K}}$

(b) The pressure of the ball,  $p$ , over time,  $t$ , varies as  $p = 1 + (p_0 - 1)e^{-kt}$

(c) The variation of the rate constant with the temperature is:

$$k(T) = k_{(298.15)} e^{\left(\frac{E_a}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)}$$

to obtain the final equation

$$p = 1 + \left(p_0 \cdot \frac{T}{298.15 \text{ K}} - 1\right) e^{-k \cdot e^{\left(\frac{E_a}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T}\right)\right)} \cdot t}$$

$$p = 1 \text{ atm} + \left(1.80 \cdot \frac{302.15 \text{ K}}{298.15 \text{ K}} - 1\right) \text{ atm} \cdot$$

$$e^{-2.88 \cdot 10^{-3} \text{ h}^{-1} \cdot e^{\left(\frac{50000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \cdot \left(\frac{1}{298.15 \text{ K}} - \frac{1}{302.15 \text{ K}}\right)\right)} \cdot 12 \text{ h}} =$$

$$= 1.74 \text{ atm}$$

**2 pt** for the correct value (**0.5 pts** for correct calculation of factor (a), **0.75 pts** for correct factor (b) and **0.75 pts** for correct factor (c)).

#### 4.5

We need to find the volume of rubber for one ball. The rubber has a thickness of 0.2 cm and it coats an inner sphere of radius 3.0 cm. Thus, the volume is:

$$V = \frac{4}{3} \pi \left( (3.2 \text{ cm})^3 - (3.0 \text{ cm})^3 \right)$$

$$= 24.16 \text{ cm}^3 \text{ 2 pt}$$

so the total mass considering the number of balls and recycling efficiency is:

$$m = 2000 \times 1.34 \text{ g cm}^{-3} \times 24.16 \text{ cm}^3 \times 0.92$$

$$= 59,589 \text{ g} = 59.6 \text{ kg} \text{ 1 pt}$$



## 5. Solar-powered multi-stage flash desalination

6.5% of the total

5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	Total
2	2	3	2	2	2	1	2	16

5.1

100 g total mass means 3.45 g NaCl and 96.55 g H<sub>2</sub>O. **0.5 pt**

Molar mass of NaCl is 58.44 g mol<sup>-1</sup>.

$$m = \frac{3.45 \text{ g}}{58.44 \text{ g mol}^{-1} \cdot 0.09655 \text{ kg}} = 0.6114 \text{ mol kg}^{-1} \quad \mathbf{0.5 \text{ pt}}$$

Assuming complete ionisation of NaCl,  $i = 2$

$$\Delta T_b = iK_b m = 2 \cdot 0.512 \text{ K kg mol}^{-1} \cdot 0.6114 \text{ mol kg}^{-1} = 0.6261 \text{ K}$$

**0.5 pt**

$$\text{New bp} = 0.6261 \text{ K} + 373.15 \text{ K} = 373.7761 \text{ K} \text{ or } 100.6261 \text{ }^{\circ}\text{C} \quad \mathbf{0.5 \text{ pt}}$$

**Total = 2 pt**

5.2

$$378.00 \text{ K} - 373.15 \text{ K} = 4.85 \text{ K} \quad \mathbf{0.5 \text{ pt}}$$

$$m = \frac{\Delta T_b}{iK_b} = \frac{4.85 \text{ K}}{2 \cdot 0.512 \text{ K kg mol}^{-1}} = 4.736 \text{ mol kg}^{-1} \quad \mathbf{0.5 \text{ pt}}$$

Assume 100 g total: x g NaCl, (100-x)g H<sub>2</sub>O

$$4.736 \text{ mol kg}^{-1} = \frac{x \text{ g}}{[58.44 \text{ g mol}^{-1}] \cdot [(100-x)\text{g}/1000 \text{ kg}]} = 21.7\%$$

**1.0 pt**

**Total = 2 pt**



### 5.3

Selection of correct values and units ( $T_1$  must be in K):

$$T_1 = 373.7761 \text{ K}; P_1 = 1.0 \text{ atm}; P_2 = 2.5 \text{ atm} \quad \mathbf{0.5 \text{ pt}}$$

$$\Delta H_{\text{vap}} = 40.716 \text{ kJ mol}^{-1} \quad \mathbf{0.5 \text{ pt}}$$

Using Clausius-Clapeyron equation:

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{2.5 \text{ atm}}{1 \text{ atm}} = -\frac{40716 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{T_2} - \frac{1}{373.7761 \text{ K}} \right) \quad \mathbf{1 \text{ pt}}$$

$$-1.8710 \cdot 10^{-4} \text{ K}^{-1} = \left( \frac{1}{T_2} - \frac{1}{373.7761 \text{ K}} \right)$$

$$2.4883 \cdot 10^{-3} \text{ K}^{-1} = \frac{1}{T_2}$$

$$T_2 = 401.88 \text{ K} = 128.73 \text{ }^\circ\text{C} \quad \mathbf{1 \text{ pt}}$$

**Total = 3 pt**

### 5.4

After mixing mass = 2 kg; temperature = 100 °C.

Let  $n$  be amount of vapourised water.

heat lost on cooling,  $Q_c$  = heat required to vapourise water,  $Q_v$

$$Q = mC_p \Delta T \quad \mathbf{0.5 \text{ pt}}$$

$$Q_c = (2 - (0.018016 \text{ mol}^{-1}) n) \text{ kg} \cdot 3850 \text{ J kg}^{-1} \text{ K}^{-1} \cdot (373.15 - 370.15) \text{ K}$$

$$\text{or } Q_c = 2 \text{ kg} \cdot 3850 \text{ J kg}^{-1} \text{ K}^{-1} \cdot (373.15 - 370.15) \text{ K}$$

**0.5 pt**

$$Q_v = n \cdot 0.018016 \text{ kg mol}^{-1} \cdot 2260 \cdot 10^3 \text{ J kg}^{-1} \quad \mathbf{0.5 \text{ pt}}$$

$$23100 - 208.0848 n \text{ mol}^{-1} = 40716.16 n \text{ mol}^{-1}$$

$$23100 = 40924.24 n \text{ mol}^{-1}$$

$$n = 0.565 \text{ mol} \quad \mathbf{0.5 \text{ pt}}$$

**Total = 2 pt**



5.5

Amount of water in initial vapour:

$$n_0 = \frac{pV}{RT} = \frac{0.69 \cdot 101325 \text{ Pa} \cdot (100 - 1) \cdot 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot (363.15 \text{ K})}$$

$$= 2.292 \text{ mol} \quad \mathbf{1 \text{ pt}}$$

After evaporation, amount of water:

$$n = 2.292 \text{ mol} + 0.565 \text{ mol} = 2.857 \text{ mol} \quad \mathbf{0.5 \text{ pt}}$$

$$p = \frac{nRT}{V} = \frac{2.857 \text{ mol} \cdot 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 370.15 \text{ K}}{(100 - 2) \cdot 10^{-3} \text{ m}^3}$$

$$= 89716 \text{ Pa} = 0.885 \text{ atm} \quad \mathbf{0.5 \text{ pt}}$$

**Total = 2 pt**

5.6

$$\Delta T = 110^\circ \text{C} - 25^\circ \text{C} = 85^\circ \text{C} \quad \mathbf{0.5 \text{ pt}}$$

$$Q = mC_p \Delta T$$

$$Q = 1 \text{ kg} \cdot 3.85 \text{ kJ kg}^{-1} \text{ K}^{-1} \cdot 85 \text{ K}$$

$$= 327.25 \text{ kJ} \quad \mathbf{1.0 \text{ pt}}$$

$$Q = \frac{327.25 \text{ kJ}}{3600 \text{ kJ kWh}^{-1}} = 0.0909 \text{ kWh} \quad \mathbf{0.5 \text{ pt}}$$

**Total = 2 pt**

5.7

$$\text{mass of pure water in sea water} = \frac{5.0000 \cdot 10^4 \text{ m}^3 \cdot 1000 \text{ kg m}^{-3}}{0.85} = 5.88 \cdot 10^7 \text{ kg} \quad \mathbf{0.5 \text{ pt}}$$

$$\text{mass of sea water} = \frac{5.88 \cdot 10^7 \text{ kg}}{0.9655} = 6.09 \cdot 10^7 \text{ kg} \quad \mathbf{0.5 \text{ pt}}$$

**Total = 1 pt**

5.8

$$\text{energy required} = 6.09 \cdot 10^7 \text{ kg} \cdot 0.0909 \text{ kWh}$$

$$= 5.536 \cdot 10^6 \text{ kWh} \quad \mathbf{0.5 \text{ pt}}$$

$$\text{energy panels provide} = \frac{5.536 \cdot 10^6 \text{ kWh}}{0.67} = 8.263 \cdot 10^6 \text{ kWh} \quad \mathbf{0.75 \text{ pt}}$$

$$\text{number of panels} = \frac{8.263 \cdot 10^6 \text{ kWh}}{2.12 \text{ kWh}} = 344,292 \quad \mathbf{0.75 \text{ pt}}$$

**Total = 2 pt**



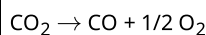


## 6. Solar energy conversion by CO<sub>2</sub> reduction

6% of the total

6.1	6.2	6.3	6.4	6.5	6.6	6.7	Total
5	2	3	3	3	2	4	22

### 6.1



Let  $n_0$  be the initial amount of CO<sub>2</sub>. At equilibrium:

$$n(\text{CO}_2) = n(\text{CO}) = 0.5n_0; n(\text{O}_2) = 0.25n_0; n_{\text{total}} = 1.25n_0.$$

$$\text{Molar fractions: } x(\text{CO}_2) = x(\text{CO}) = 0.5n_0 / 1.25n_0 = 0.4; x(\text{O}_2) = 0.2$$

$$\text{Partial pressures: } p(\text{CO}_2) = p(\text{CO}) = 0.4 \text{ bar}; p(\text{O}_2) = 0.2 \text{ bar}.$$

$$\text{Equilibrium constant: } K_p = \frac{p(\text{CO})p(\text{O}_2)^{1/2}}{p(\text{CO}_2)} = \frac{0.4 \cdot 0.2^{1/2}}{0.4} = 0.447$$

Enthalpy and entropy of the reaction:

$$\Delta_r H^\circ_{298} = (-110.5 \text{ kJ mol}^{-1}) - (-393.5 \text{ kJ mol}^{-1}) = 283 \text{ kJ mol}^{-1},$$

$$\Delta_r S^\circ_{298} = 197.7 \text{ J mol}^{-1} \text{ K}^{-1} + 0.5 \cdot 205.1 \text{ J mol}^{-1} \text{ K}^{-1} - 213.8 \text{ J mol}^{-1} \text{ K}^{-1} = 86.45 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$K_p = 0.447 = e\left(-\frac{\Delta_r G^\circ}{RT}\right) = e\left(-\frac{\Delta_r H^\circ}{RT}\right)e\left(\frac{\Delta_r S^\circ}{R}\right)$$

$$0.447 = e\left(-\frac{283000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} T}\right)e\left(\frac{86.45 \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\right)$$

$$T = 3038 \text{ K}$$

Reaction equation – **1 pt**

(reaction with integer coefficients and the corresponding calculations are also accepted)

Equilibrium composition (molar fractions) – **1 pt**

The value of the equilibrium constant – **1 pt**

Enthalpy and entropy of reaction – **0.5 pt each**

Temperature – **1 pt**

**Total – 5 pts**



## 6.2

**Reaction 1:**  $\text{Zn} + \text{CO}_2 \rightarrow \text{ZnO} + \text{CO}$

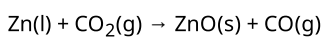
**Reaction 2:**  $\text{ZnO} \rightarrow \text{Zn} + \frac{1}{2}\text{O}_2$

Each equation – **1 pt**

**Total – 2 pts**

## 6.3

Zinc is liquid at 1073 K.



$$\Delta_r H^\circ = ((-350.5) + (-110.5) - 6.5 - (-393.5)) \text{ kJ mol}^{-1} = -74 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = (43.7 + 197.7 - 50.8 - 213.8) \text{ J mol}^{-1} \text{ K}^{-1} = -23.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r G^\circ_{1073} = -74 \text{ kJ mol}^{-1} - (-23.2 \cdot 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \cdot 1073 \text{ K} = -49.1 \text{ kJ mol}^{-1}$$

$$K = e\left(-\frac{\Delta_r G^\circ}{RT}\right) = e\left(\frac{49100 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 1073 \text{ K}}\right) = 246 = \frac{x}{1-x}$$

where x is the degree of conversion.

$$x = \frac{K}{K+1} = 0.996$$

Gibbs energy – **1 pt (0 pts if calculated with Zn(s))**

Equilibrium constant – **1 pt**

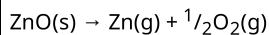
Degree of conversion – **1 pt**

**Total – 3 pts**



#### 6.4

Zinc is a gas at 2000 K.



$$\Delta_r H^\circ = (130.4 - (-350.5)) \text{ kJ mol}^{-1} = 480.9 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = (161.0 + 0.5 \cdot 205.1 - 43.7) \text{ J mol}^{-1} \text{ K}^{-1} = 219.85 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r G^\circ_{2000} = 480.9 \text{ kJ mol}^{-1} - 219.85 \cdot 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \cdot 2000 \text{ K} = 41.2 \text{ kJ mol}^{-1}$$

$$K_p = e^{\left(-\frac{\Delta_r G^\circ}{RT}\right)} = e^{\left(-\frac{41200 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 2000 \text{ K}}\right)} = 0.084$$

$$K_p = p(\text{Zn})p(\text{O}_2)^{\frac{1}{2}} = 2p(\text{O}_2)p(\text{O}_2)^{\frac{1}{2}} = 2p(\text{O}_2)^{\frac{3}{2}}$$

$$p(\text{O}_2) = 0.12 \text{ bar}$$

Gibbs energy – **1 pt (0 pts if calculated with Zn(s))**

The value of equilibrium constant – **1 pt**

Pressure of oxygen – **1 pt (0 pts if calculated with Zn(s))**

**Total – 3 pts**

#### 6.5

+3	+2 (anion)	+2 (molecule)	0	-2	-4
CO <sub>2</sub> <sup>-</sup> or HCO <sub>2</sub> <sup>-</sup> or CO <sup>+</sup>	HCOO <sup>-</sup> or CO <sub>2</sub> <sup>2-</sup>	CO or HCOOH	CH <sub>2</sub> O or CH <sub>2</sub> (OH) <sub>2</sub>	CH <sub>3</sub> OH or CH <sub>3</sub> O <sup>-</sup> or CH <sub>3</sub> <sup>+</sup>	CH <sub>4</sub>

**0.5 pts** for each correct formula. Any reasonable suggestion is accepted.  
**Total – 3 pts**



6.6

CdS ✓	Ge ✓	Si ✓	SiC	WO <sub>3</sub> ✓	ZrO <sub>2</sub>
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Calculations:

$$\lambda = 400 \text{ nm}$$

$$E(eV) = \frac{hc}{\lambda} = \frac{1.602 \cdot 10^{-19} \text{ J} \cdot \text{eV}^{-1}}{400 \cdot 10^{-9} \text{ m} \cdot 1.602 \cdot 10^{-19} \text{ J} \cdot \text{eV}^{-1}} = 3.10 \text{ eV}$$

Semiconductors with a band gap of less than 3.10 eV can be excited by visible light.

**0.25 pt** for each correct choice, penalty **0.5 pt** for each wrong choice down to zero.

**1 pt** for the calculation supporting the choice.

**Total – 2 pts**

6.7

Calculations:

$$\text{Quantity of CO}_2: n(\text{CO}_2) = pV / RT$$

$$= 101.325 \text{ kPa} \cdot 3.0 \text{ L} \cdot \text{min}^{-1} \cdot 420 \text{ min} / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K}) = 51.5 \text{ mol}$$

Degree of CO<sub>2</sub> conversion:

$$\eta = (n(\text{HCHO}) + n(\text{CH}_3\text{OH})) / n(\text{CO}_2)$$

$$= (1.0 \cdot 10^{-3} \text{ M} + 5.4 \cdot 10^{-3} \text{ M}) \cdot 0.1 \text{ dm}^3 / 51.5 \text{ mol}$$

$$= 1.2 \cdot 10^{-5}$$

Quantity of photons:

$$n(h\nu) = Pt / E_m = Pt / (hcN_A / \lambda) = Pt\lambda / hcN_A$$

$$= 500 \text{ W} \cdot 7 \cdot 3600 \text{ s} \cdot 365 \cdot 10^{-9} \text{ m} / (6.626 \cdot 10^{-34} \text{ J s} \cdot 2.998 \cdot 10^8 \text{ m s}^{-1} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1})$$

$$= 38.4 \text{ mol}$$

Formation of HCHO and CH<sub>3</sub>OH from CO<sub>2</sub> requires 4 and 6 electrons, respectively.

Apparent quantum yield:

$$\phi = (4n(\text{HCHO}) + 6n(\text{CH}_3\text{OH})) / n(h\nu) = (4 \cdot 1.0 \cdot 10^{-3} \text{ M} + 6 \cdot 5.4 \cdot 10^{-3} \text{ M}) \cdot 0.1 \text{ dm}^3 / 38.4 \text{ mol} = 9.5 \cdot 10^{-5}$$

With conventional semiconductors, both the degree of conversion and quantum yield of photocatalysis are very low.

Each calculation – **1 pt**

**Total – 4 pts**

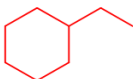





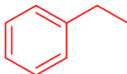
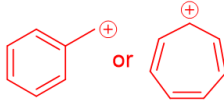


## 7. Dubai crude oil

7% of the total

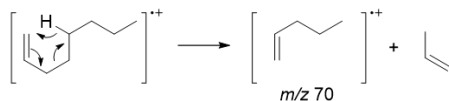
7.1	7.2	7.3	7.4	7.5	Total
8	2	3	1	8	22

7.1

<b>1</b>  (N, C <sub>8</sub> H <sub>16</sub> )	<b>1'</b> 
<b>2</b>  (P, C <sub>8</sub> H <sub>18</sub> )	<b>2'</b> 
<b>3</b>  (O, C <sub>8</sub> H <sub>16</sub> )	<b>3'</b> 
<b>4</b>  (A, C <sub>8</sub> H <sub>10</sub> )	<b>4'</b> 

Based on the mass spectra, compounds **1–4** have (relative) molecular masses of 112, 114, 112, and 106, respectively. The molecular mass of 114 corresponds to an alkane with the formula C<sub>8</sub>H<sub>18</sub>, indicating that **2** is an alkane (**P**), specifically *n*-octane, as it is a linear alkane. Fragmentation product **2'** has *m/z* 43, corresponding to a propyl or isopropyl cation.

The molecular mass of 112 corresponds to hydrocarbons with the molecular formula C<sub>8</sub>H<sub>16</sub>. Therefore, **1** and **3** are an alkene (**O**) and a cycloalkane (**N**). The only linear alkene without *cis-trans* isomers is oct-1-ene. Comparing the mass spectra of **1** and **3**, one could notice that the mass spectrum for **1** is missing the [M–15]<sup>+</sup> peak, which corresponds to the loss of a methyl group. This peak should be present for a linear alkene, confirming that **3** is oct-1-ene. Alternatively, one could also use the hint that **3'** (*m/z* 70) is formed by a McLafferty rearrangement, which requires the presence of a double bond:





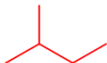

Since **3** is an alkene, **1** is a monosubstituted cycloalkane (**N**) with the molecular formula  $C_8H_{16}$ . Given that the base peak **1'** in the mass spectrum is  $[M-29]^+$ , this suggests that the substituent is an ethyl group. Consequently, **1** is ethylcyclohexane, as when an ethyl group is removed, a stable secondary cation is formed.

Finally, **4** is an arene (**A**) with the formula  $C_8H_{10}$ . This could correspond to ethylbenzene or one of the dimethylbenzene isomers. The base peak **4'** is  $[M-15]^+$ , indicating the loss of a methyl group. Therefore, **4** is ethylbenzene, as when a methyl is removed, a stabilised benzyl cation, which can rearrange into the aromatic tropylium cation, is produced.

For compounds **1-4**: **1 pt** per correct structure. If the structure is incorrect, then **0.25 pt** in case the molecular formula is correct, and **0.25 pt** in case the compound is of the same class as the correct one. If no structure is given, then **0.25 pt** for the molecular formula and **0.25 pt** for the letter.

For fragments **1'-4'**: **1 pt** per correct structure. If the structure is incorrect, then **0.25 pt** in case the molecular formula is correct, and an additional **0.25 pt** in case "+" or "-+" is also given.

## 7.2

<b>5</b> 	<b>6</b> 
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The mass spectrum of **5** shows a molecular peak at  $m/z$  72, which corresponds to  $C_5H_{12}$ . Pentane has only two branched isomers: 2-methylbutane and 2,2-dimethylpropane. The base peak for **5** is  $[M-29]^+$ , which corresponds to loss of an ethyl group. Therefore, **5** is 2-methylbutane, as only this branched isomer contains an ethyl group.

At first glance, the mass spectrum of **6** appears to have a molecular ion peak  $[M]^+$  at  $m/z$  57, as it is the rightmost peak, along with the  $[M+1]^+$  peak due to  $^{13}C$ . However, since alkanes cannot have an odd molecular mass, this peak corresponds instead to the  $C_4H_9^+$  cation. What happens is that the molecular ion peak in the mass spectrum of **6** is so weak that it is not visible within the given scale. However, since the  $[M+1]^+$  peak has an intensity of ca. 5.4% relative to  $[M]^+$ , one can determine that compound **6** contains  $5.4/1.1 \approx 5$  carbon atoms. Therefore, **6** is the second branched isomer of pentane, 2,2-dimethylpropane. The low molecular peak intensity is explained by the formation of a highly stable *tert*-butyl cation upon methyl loss, which favours fragmentation of the molecular ion.

Compound **5**: **1 pt** for the correct structure. **0.5 pt** if only the correct molecular formula is given.

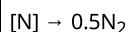
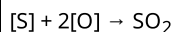
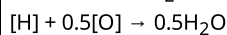
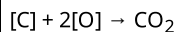
Compound **6**: **1 pt** for the correct structure. **0.5 pt** if 2,2,3,3-tetramethylbutane is given instead of 2,2-dimethylpropane. **0.5 pt** if only the correct molecular formula is given.

**1 pt** total if structures **5** and **6** are switched.

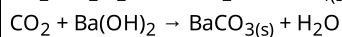
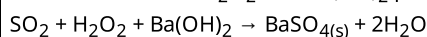


### 7.3

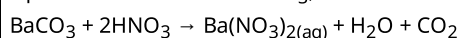
The combustion of oil gives the following products:



The reactions with  $H_2O_2$  and  $Ba(OH)_2$  proceed as follows:



Upon acidification with  $HNO_3$ , the carbonate precipitate dissolves:



Since only  $BaSO_4$  remains as the final precipitate (**1 pt**), we can determine the sulfur content as follows:

$$n(BaSO_4) = (1 - 0.9895) \cdot 1.395 \text{ g} / 233.39 \text{ g mol}^{-1} = 6.276 \cdot 10^{-5} \text{ mol} = n(S) \text{ (1 pt)}$$

$$w(S) = 6.276 \cdot 10^{-5} \text{ mol} \cdot 32.06 \text{ g mol}^{-1} / (115 \cdot 10^{-6} \text{ dm}^3 \cdot 871 \text{ g dm}^{-3}) \cdot 100\% = 2.01 \text{ wt.\%} \Rightarrow \text{sour oil (1 pt)}$$

### 7.4

<input type="checkbox"/> 270 nm	<input type="checkbox"/> 300 nm	<input checked="" type="checkbox"/> 350 nm	<input type="checkbox"/> 510 nm
The optimal wavelength for absorbance measurements is 350 nm, as both <b>X</b> and <b>Y</b> absorb the most light at this wavelength. ( <b>1 pt</b> )			



## 7.5

Selenite ( $\text{SeO}_3^{2-}$ ) is selectively determined via piazoselenol ( $\text{Y}$ ) formation. This reaction's efficiency depends on pH, as seen in the  $S(\text{X})/S(\text{Y})$  ratio variations in the table: at low  $\text{H}^+$  concentrations, the reaction does not reach completion, while at high  $\text{H}^+$  concentrations, diamine ( $\text{X}$ ) protonation or the formation of selenium side products occurs.

We have acids with different properties:

- $\text{HNO}_3$  is a strong oxidiser, so  $\text{SeO}_3^{2-}$  is oxidised to  $\text{SeO}_4^{2-}$ . This is why the  $S(\text{X})/S(\text{Y})$  is high, as there is minimal piazoselenol ( $\text{Y}$ ) formation.
- On the other side,  $\text{HI}$  is a strong reducing agent, which seems to reduce  $\text{SeO}_3^{2-}$  (and  $\text{SeO}_4^{2-}$ ) possibly to  $\text{Se}$ , again preventing piazoselenol ( $\text{Y}$ ) formation and leading to increased  $S(\text{X})/S(\text{Y})$  ratios.
- $\text{HCl}$  and  $\text{HBr}$  provide optimal conditions (**1 pt**), stabilising the  $S(\text{X})/S(\text{Y})$  ratio in the middle of the pH range. The  $S(\text{X})/S(\text{Y})$  of 0.523 obtained in  $\text{HCl}$  corresponds to the initial  $\text{SeO}_3^{2-}$  content, while the ratio of 0.368 in  $\text{HBr}$  corresponds to the combined  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  content, as  $\text{SeO}_4^{2-}$  is reduced to  $\text{SeO}_3^{2-}$  by  $\text{HBr}$ .

From the blank experiment, the peak area of  $\text{X}$  is 0.825 min mAbs, and its concentration after dilution is:  $300 \mu\text{M} \cdot 0.50 \text{ mL} / (9.50 \text{ mL} + 0.50 \text{ mL}) = 15.0 \mu\text{M}$ . Thus, the proportionality constant between peak area and the concentration of  $\text{X}$  is:  $0.825 \text{ min mAbs} / 15.0 \mu\text{M} = 0.0550 \text{ min mAbs } \mu\text{M}^{-1}$  (**1 pt**).

Since the total concentration of  $\text{X}$  and  $\text{Y}$  is  $15.0 \mu\text{M}$ , and  $\text{Y}$  represents the selenite ( $\text{SeO}_3^{2-}$ ) concentration, we set up the following system of equations:

For  $\text{HCl}$  medium:

$$[\text{X}]_{\text{HCl}} + [\text{SeO}_3^{2-}] = 15.0 \text{ (1 pt)}$$

$$0.523 = 0.0550 \cdot [\text{X}]_{\text{HCl}} / (1.21 \cdot [\text{SeO}_3^{2-}]) \text{ (1 pt)}$$

For  $\text{HBr}$  medium, where additional  $\text{SeO}_3^{2-}$  was formed due to reduction of  $\text{SeO}_4^{2-}$ :

$$[\text{X}]_{\text{HBr}} + [\text{SeO}_3^{2-}] + [\text{SeO}_4^{2-}] = 15.0 \text{ (1 pt)}$$

$$0.368 = 0.0550 \cdot [\text{X}]_{\text{HBr}} / (1.21 \cdot ([\text{SeO}_3^{2-}] + [\text{SeO}_4^{2-}])) \text{ (1 pt)}$$

Solving these equations, we obtain:

$$[\text{SeO}_3^{2-}] = 1.20 \mu\text{M}, [\text{SeO}_4^{2-}] = 0.45 \mu\text{M} \text{ (1 pt)}$$

Before dilution:

$$c(\text{SeO}_3^{2-})_0 = 1.20 \mu\text{M} \cdot 10 \text{ mL} / 9.5 \text{ mL} = 1.26 \mu\text{M}, c(\text{SeO}_4^{2-})_0 = 0.45 \mu\text{M} \cdot 10 \text{ mL} / 9.5 \text{ mL} = 0.47 \mu\text{M} \text{ (1 pt)}$$

### References:

All mass spectra were sourced from: NIST Standard Reference Database 69: NIST Chemistry WebBook (<https://webbook.nist.gov/>)





## 8. Carbon monoxide: deadly poison or promising therapeutic agent?

7.5% of the total

8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	Total
4	1	6	3	2	2	4	8	5	35

8.1

		Ox	Red	Same
(a)	$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$	✓		
(b)	$\text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right) \text{O}_2 \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O}$	✓		
(c)	$\text{NO}_x \rightarrow \frac{1}{2}\text{N}_2 + \frac{x}{2}\text{O}_2$		✓	
<p><b>0.5 pt</b> reaction in (a). <b>1 pt</b> for reaction in (b) and <b>1 pt</b> for reaction in (c). <b>0.5 pt</b> for each correct tick. <b>Total = 4 pts</b></p>				

8.2

$10 \text{ mL min}^{-1} \text{ CO} = 5 \text{ mL min}^{-1} \text{ O}_2 = 25 \text{ mL min}^{-1} \text{ air}$
<b>1 pt</b>



### 8.3

volume of CO = 60 min  $\times$  0.01 dm<sup>3</sup> min<sup>-1</sup> = 0.6 dm<sup>3</sup> **1pt**

amount of CO,  $n = \frac{pV}{RT} = \frac{101325 \text{ Pa} \times 0.6 \times 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 273.15 \text{ K}} = 0.02677 \text{ mol}$  **1pt**

amount of CO<sub>2</sub> = 0.02677 mol  $\times$  0.7 = 0.01874 mol

molecules of CO<sub>2</sub> = 0.01874 mol  $\times$  6.022  $\times$  10<sup>23</sup> mol<sup>-1</sup> = 1.128  $\times$  10<sup>22</sup> **1pt**

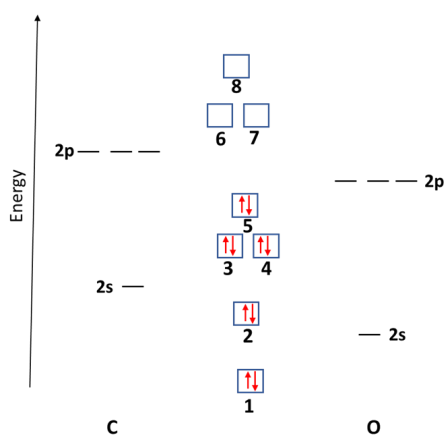
mass of Pd at surface : 0.1 g  $\times$  0.1  $\times$  0.1 = 0.001 g **1pt**

atoms of Pd at surface =  $\frac{0.001 \text{ g}}{106.42 \text{ g mol}^{-1}} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 5.659 \times 10^{18}$  **1pt**

molecules CO<sub>2</sub> per surface Pd atom =  $\frac{1.128 \times 10^{22}}{5.659 \times 10^{18}} = 1.99 \times 10^3$  **1pt**

**Total = 6 pts**

### 8.4



MO	1	2	3	4	5	6	7	8
Type of overlap	$\sigma$	$\sigma$	$\pi$	$\pi$	$\sigma$	$\pi$	$\pi$	$\sigma$

**1.5 pts** for the type of overlap, **0.25 pt** each. Adding the (\*) for antibonding is not a must and no marks for its addition.

**1.5 pts** for filling the electrons in the orbitals correctly with spins correct. If the number of electrons is correct but the electrons are not in the correct orbitals or spins are wrong/not indicated **0.5 pt**.

**Total = 3 pts**

### 8.5



	in	dec	nc
Ru-CO	✓		
C-O		✓	

1 pt each  
Total = 2 pts



8.6

	1850 cm <sup>-1</sup>	1930 cm <sup>-1</sup>	2100 cm <sup>-1</sup>	2143 cm <sup>-1</sup>
A			✓	
B		✓		
C	✓			
CO				✓

0.5 pt for each correctly assigned wavenumber.

Total = 2 pts

8.7

volume of adsorbed CO = 50 μL × 0.1 × (0.96 + 0.90 + 0.80 + 0.50 + 0.20)

= 16.8 μL **1 pt**

Molecules of adsorbed CO:

amount of CO,  $n = \frac{100000 \text{ Pa} \times 1.68 \times 10^{-8} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} \times 6.022 \times 10^{23} \text{ mol}^{-1}$

=  $4.08 \times 10^{17}$  **1 pt**

Ni surface atoms =  $4.08 \times 10^{17}$

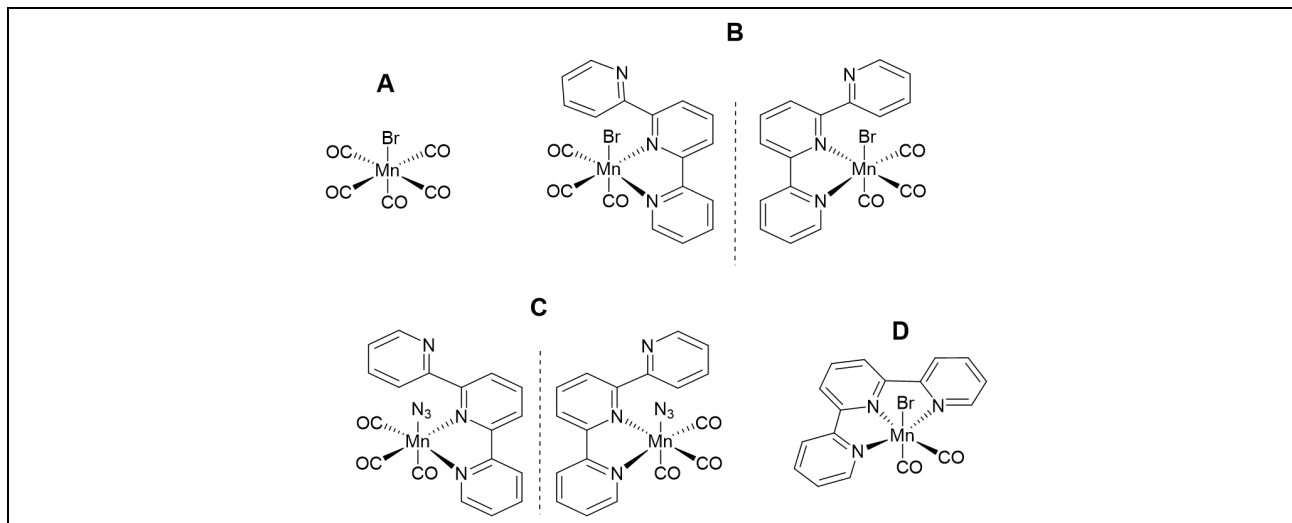
total Ni atoms =  $0.015 \text{ g} \times 0.1 \times \frac{6.02 \times 10^{23} \text{ mol}^{-1}}{58.69 \text{ g mol}^{-1}} = 1.54 \times 10^{19}$  **1 pt**

% exposed on surface =  $\frac{4.08 \times 10^{17}}{1.54 \times 10^{19}} \times 100\% = 2.65\%$  **1 pt**

Total = 4 pts



8.8



**A** Correct **1 pt**.  $\text{Mn}(\text{CO})_5\text{Br}$  formula only **0.5 pt**.

**B** correct *fac* with shape clear **3 pts** (only one enantiomer is needed). **B** correct but with unclear/ambiguous shape drawing **2.0 pts**. Structures that satisfy the correct formula are given **0.5 pt** (This is for formula only, a *mer* structure, or a structure with a non-coordinated Br). Any structure that does not match formula **0 pt**.

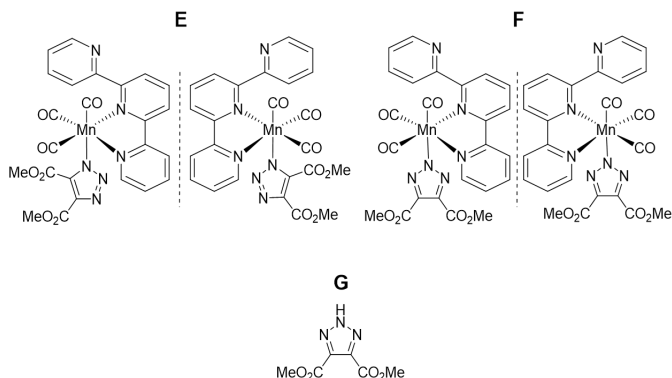
**C** correct *fac* with shape clear **2 pts** (only one enantiomer is needed). **C** correct but with unclear/ambiguous shape drawing **1.5 pts**. Structures that satisfy the correct formula are given **0.5 pt** (This is for formula only, a *mer* structure, or a structure with a non-coordinated azide). Any structure that does not match formula **0 pt**. No error carried forward from **B** as new data given.

**D** correct *cis* with shape clear **2 pts**. **D** correct but with unclear/ambiguous shape drawing **1.5 pts**. Structures that satisfy the correct formula are given **0.5 pt** (This is for formula only, a *trans* structure, or a five-coordinated structure with a non-coordinated azide). Any structure that does not match formula **0 pt**. No error carried forward from **B** as new data given.

**Total = 8 pts**



8.9



**E** Correct **2 pts**. Either enantiomer is fine. Full credit can be given for error carried forward structures from **C** if ligands around Mn have been kept the same, however, triazole must be drawn correctly and coordinated through correct N **2 pt**. Change in ligands around Mn but triazole correct and correctly coordinated **1 pt**. If compound **F** has been drawn here **1 pt**.

**F** Correct **2 pts**. Either enantiomer is fine. Full credit can be given for error carried forward structures from **C/E** if ligands around Mn have been kept the same, however, triazole must be drawn correctly and coordinated through correct N **2 pt**. Change in ligands around Mn but triazole correct and correctly coordinated **1 pt**. If compound **E** has been drawn here **1 pt**.

**G** Correct **1 pt**. Wrong triazole NH isomer **0.5 pt**. Error carried forward can be given from **F** if wrong triazole is drawn there but consistent here **1 pt**.

**Total = 5 pts**

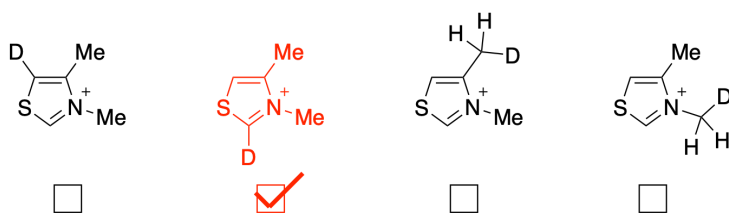


## 9. Enzymes and cofactors

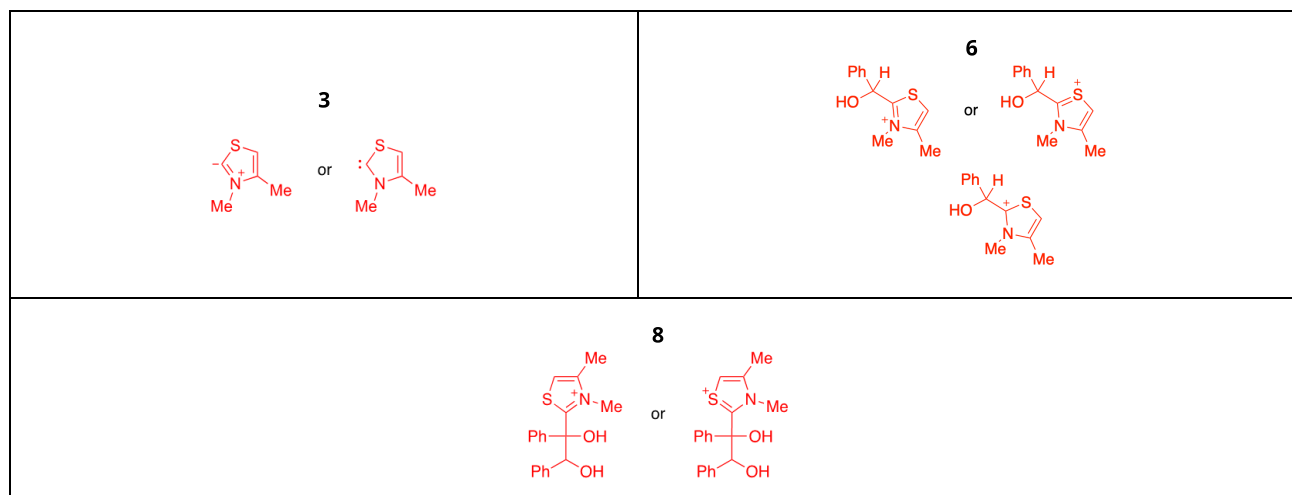
7% of the total

9.1	9.2	9.3	9.4	9.5	9.6	Total
2	6	2	6	10	12	38

9.1 (2 pt)



9.2 (6 pt)



2 pt for each structure.

Intermediate **3** is graded with **2 pt** and intermediate **6** is graded with **1 pt** if deuteration was performed at the wrong position in 9.1 and the same wrong assumption was made for compounds **3** and **6**.

-0.5 pt if a charge is missed.

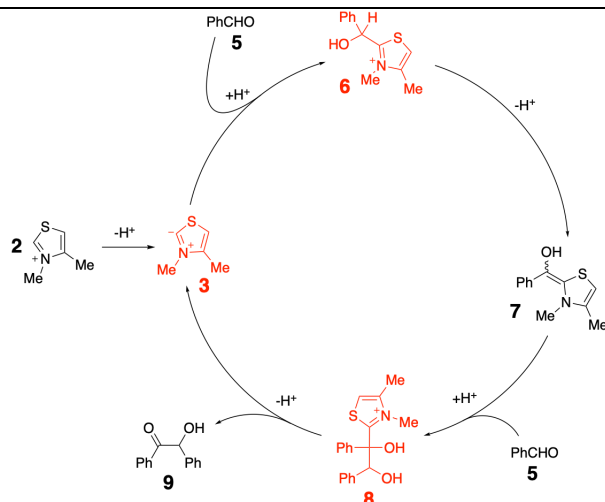
Alternative but correct resonance structures are graded with full points.

**6 pt total**

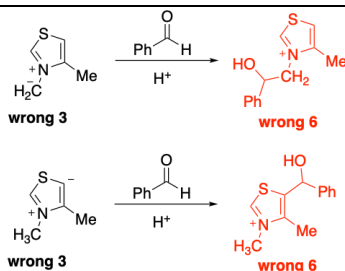
The completed catalytic cycle is presented below.



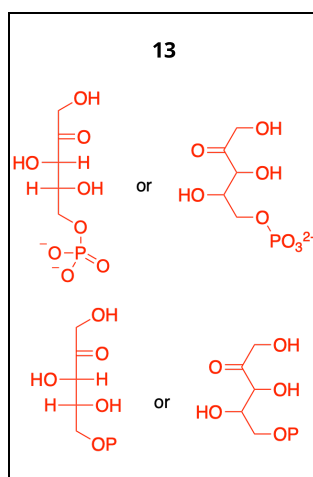
أولمبياد الكيمياء الدولي السابع والخمسون  
الإمارات العربية المتحدة  
57<sup>th</sup> IChO - United Arab Emirates - 2025



For error carried forward, if a wrong atom is deprotonated in compound **2** (e.g., methyl group, see structure “**wrong 3**” below); then structure “**wrong 6**” is graded partially (**1 pt**) since the same mistake is conserved and chemistry makes sense, however only partial point is given since this structure cannot lead to intermediate **7**.



9.3 (2 pt)



**2 pt** total regardless of the stereochemistry; **0.5 pts** if one charge is missing (charge is not required in case of phosphate being abbreviated as “P”).





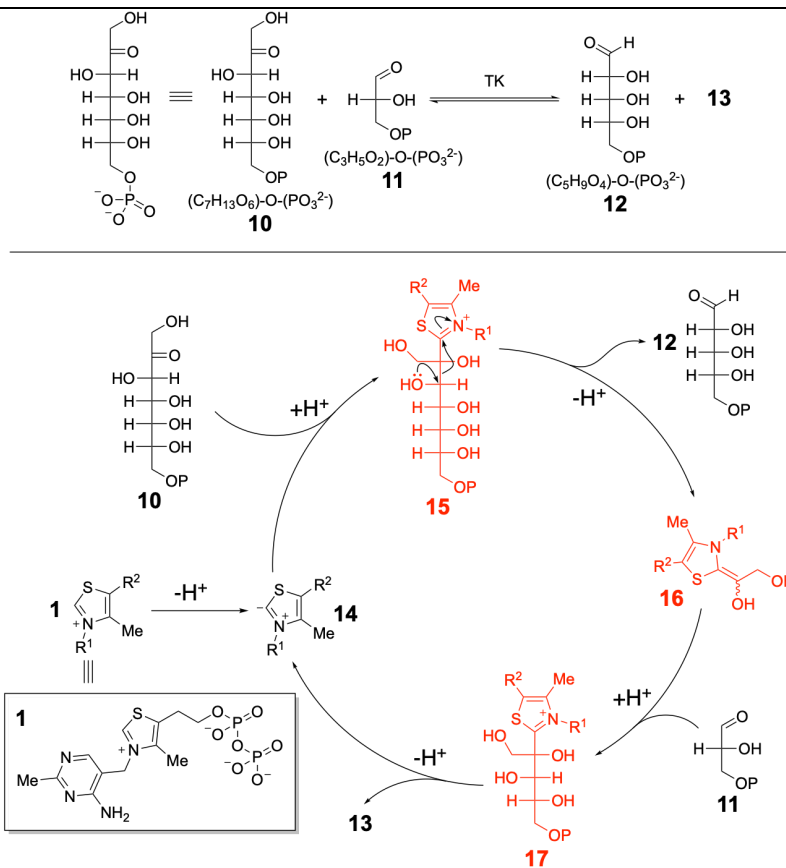
9.4 (6 pt)

<p style="text-align: center;"><b>15</b></p>	<p style="text-align: center;"><b>16</b></p>
<p style="text-align: center;"><b>17</b></p>	
<p><b>2 pt</b> each (stereochemistry is not graded) Alternative but correct resonance structures are graded with full points. <b>6 pts total</b></p>	

The complete catalytic cycle is presented below.



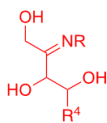
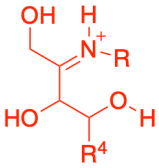
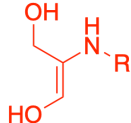
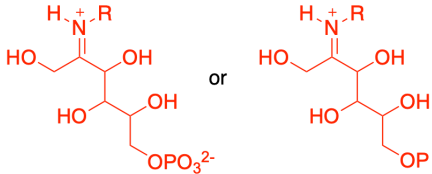
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Error carried forward scoring can be given in a similar manner to previously.



9.5 (10 pt)

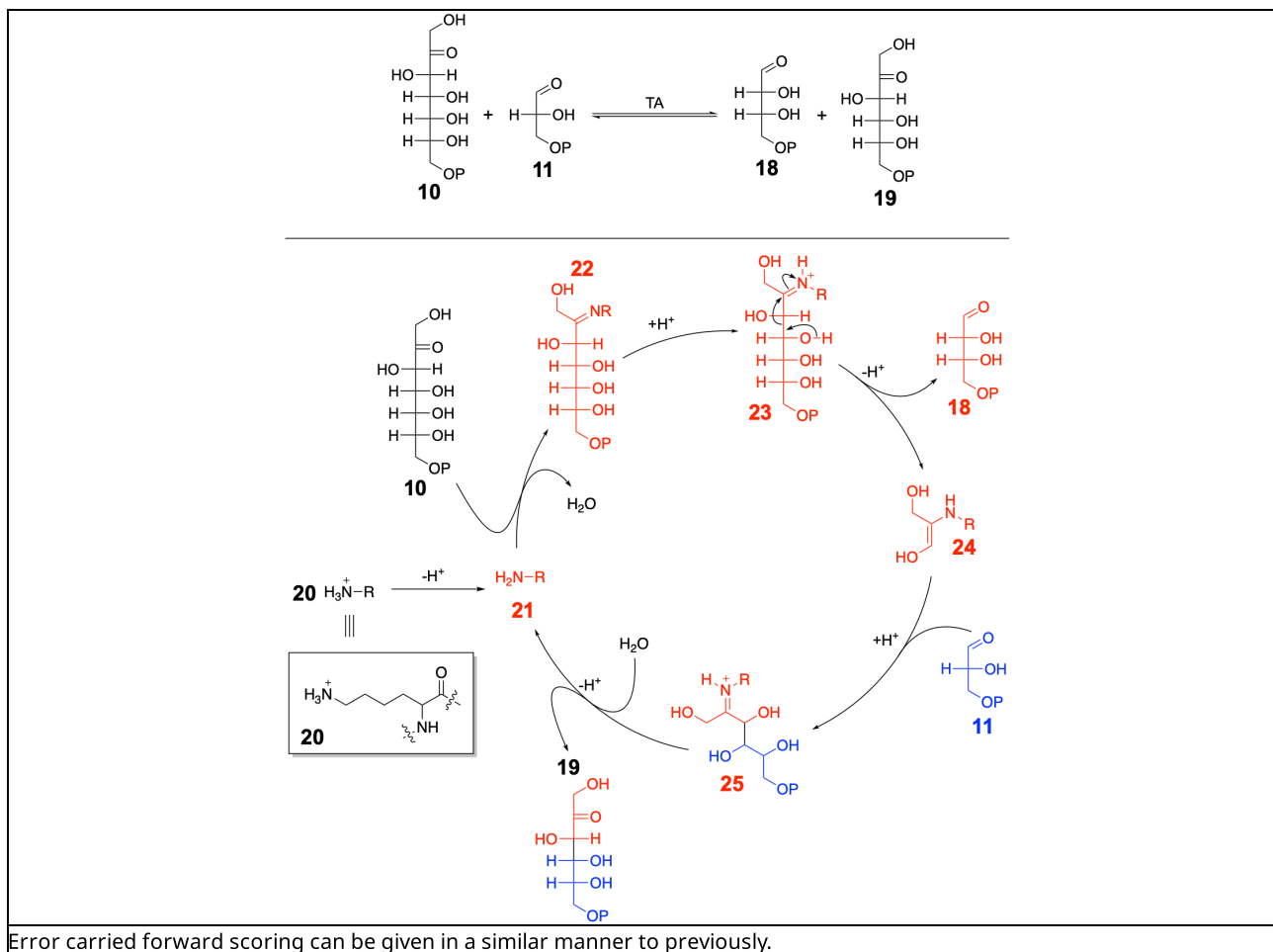
<p>21</p> <p><math>\text{H}_2\text{N}-\text{R}</math></p>	<p>22</p> 
<p>23</p> 	<p>24</p> 
<p>25</p> 	

**2 pt** each (stereochemistry is not graded). If the charge is missed, penalty of -0.5 pt is applied.  
Alternative but correct resonance structures are graded with full points.

**10 pts total**



The complete catalytic cycle is presented below.

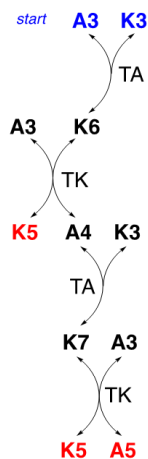


Error carried forward scoring can be given in a similar manner to previously.



9.6 (12 pt)

The correct scheme is shown with blue 3-carbon starting sugars and red 5-carbon sugar products. The TK reaction is the only option for K6+A3, as the TA reaction would lead to products equivalent to the starting materials (A3+K3). A4 can only react with K3 affording K7. The latter reacts with A3 through the TK reaction leading to two 5-carbon products (in case of the TA reaction the products would be 4- and 6-carbon sugars and not 5-carbon sugars).



2.5 pt for each correct step, if correct substrates, correct product(s), and correct enzyme are given. Mistake in one of the three above results in 2 pt, mistake in two of the three above results in 1 pt.

10 pt total

Alternative correct solutions will also get full marks.