



أولمبياد الكيمياء الدولي السابع والخمسون
الإمارات العربية المتحدة
57th ICHO - United Arab Emirates - 2025

Preparatory problems for the 57th International Chemistry Olympiad 2025

United Arab Emirates

Preface

The Scientific Committee of the 57th International Chemistry Olympiad is pleased to announce the release of the preparatory problems for IChO 2025, scheduled to take place in the United Arab Emirates in July 2025. These problems are designed to help students prepare for the Olympiad by aligning both theoretical and practical components with the core IChO syllabus (available at www.ichosc.org/regulations, Appendix C), while minimising content that extends beyond it. However, this year's preparatory problems also include advanced topics, as detailed in the problem set.

For 2025, the Scientific Committee has prepared 30 theoretical problems and 7 practical tasks that showcase the breadth and diversity of chemistry. These problems are intended to challenge and inspire participants, reflecting the complexity and style of the final exam. Although the problems are extensive, they are crafted to provide a valuable learning experience. Mentors are encouraged to share feedback or questions by reaching out to info@icho2025.ae.

This global scientific event offers young minds an opportunity to expand their knowledge of chemistry while inspiring and learning from one another. Beyond promoting careers in fundamental sciences, the competition highlights the importance of chemistry as a key scientific discipline. Participants will also experience the unique culture and history of the UAE while forging connections with peers from around the world.

The Scientific Committee of the 57th International Chemistry Olympiad
United Arab Emirates, January 2025

Acknowledgements

We extend our deepest gratitude to the authors who contributed to the preparatory and competition problems for the 57th International Chemistry Olympiad. Their months of dedicated work have culminated in a comprehensive resource to support the young chemists participating in the event. We also thank the IChO Steering Committee members, scientific reviewers, and language proofreaders for their invaluable contributions to this effort.



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Fields of advanced difficulty

Theoretical

1. **Stereochemistry** Newman projections; models for control of addition of new stereocentres (Felkin-Anh, Zimmerman-Traxler); geometrical isomers of square planar and octahedral transition metal complexes; recognising isomer possibilities in molecules with multiple stereocentres.
2. **Enzymes** Enzyme classification according to reaction types; isotope-labelling studies; metabolic pathways involving coenzyme A.
3. **Phase and chemical equilibria** Latent heats and the Clausius-Clapeyron equation; colligative properties; temperature dependence of equilibrium constants.
4. **Analytical techniques** Mass spectrometry (molecular ions, fragmentation, isotope distribution); interpretation of IR data.
5. **Photochemistry** Photocatalysis; band gaps; quantum yields; semiconductors.
6. **MO theory** MO diagrams for diatomics; metal-ligand interactions.

The following topics will not appear at IChO 2025:

- Formal group theory
- Planar, axial, or helical chirality
- Enzymatic kinetics
- Quantitative understanding of any isotope effects
- Kinetics of complex reactions
- Steady state and quasi equilibrium approximations
- NMR spectroscopy
- Synthetic polymers
- Photocatalytic organic mechanisms
- Pericyclic organic mechanisms
- Crystal field theory
- Thermodynamics and kinetics of adsorption
- Solid state crystal structures

Students are not expected to:

- Remember metabolic pathways by heart



Practical

1. **Vacuum filtration**
2. **Thin layer chromatography**
3. **Microscale reactions** Use of a micropipette and a 96 well plate

The following topics will not appear at IChO 2025:

- Extraction with immiscible solvents
- Determination of magnetic moments

Students are not expected to:

- Use a spectrophotometer themselves

References and credits for these preparatory problems are included in the answer guide for mentors.



Periodic table and data sheet

It is the intention of the Scientific Committee that the Final Exam will have the same data sheet of physical constants and formulae as the Preparatory Problems.

Physical constants and formulae

Avogadro constant	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
molar gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	F	96485 C mol^{-1}
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
speed of light in vacuum	c	$2.998 \times 10^8 \text{ m s}^{-1}$
mass of electron	m_e	$9.109 \times 10^{-31} \text{ kg}$
charge of electron	e	$1.602 \times 10^{-19} \text{ C}$
atmospheric pressure	p_{atm}	101325 Pa
ionic product of water at 298 K	K_w	10^{-14}

$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$
$1 \text{ Å} = 1 \times 10^{-10} \text{ m}$
$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$
$0 \text{ °C} = 273.15 \text{ K}$



area of triangle	$A = \frac{1}{2}ab \cdot \sin C$
volume of cube	$V = a^3$
volume of sphere	$V = \frac{4}{3}\pi r^3$
surface area of sphere	$S = 4\pi r^2$
volume of cylinder	$V = \pi r^2 h$
ideal gas equation	$pV = nRT$
frequency of light	$\nu = \frac{c}{\lambda}$
energy of a photon	$E = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log \frac{I_0}{I} = \varepsilon cl$
spin only magnetic moment	$\mu = \sqrt{n(n+2)} \text{ BM}$
Henderson-Hasselbalch equation	$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$
0 th order integrated rate law	$[\text{A}] = [\text{A}]_0 - kt$
1 st order integrated rate law	$\ln[\text{A}] = \ln[\text{A}]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-\frac{E_a}{RT}}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_r G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$
Clausius-Clapeyron equation	$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
Raoult's law	$p_i = x_i p_i^*$
boiling point elevation	$\Delta T = i K_b m$
freezing point depression	$\Delta T = i K_f m$

Consider all gases ideal unless told otherwise.

In equilibrium constant calculations, all concentrations are referenced to a concentration of 1 mol dm⁻³.



IR absorption data

Bond stretching frequencies

Bond type		Wavenumber (cm ⁻¹)
C-H	Alkane	3000-2850
	Alkene	3100-3000
	Aromatic	3150-3050
	Alkyne	~3300
	Aldehyde	2900-2700
C=C	Alkene	1680-1600
	Aromatic	1600-1400
C≡C	Alkyne	2250-2100
C=O	Aldehyde	1740-1720
	Ketone	1725-1705
	Carboxylic acid	1725-1700
	Ester	1750-1720
	Amide	1670-1640
	Anhydride	1810, 1760
C-O	Alcohol, ether, ester, carboxylic acid, anhydride	1300-800
O-H	Alcohol, phenol, free	3600-3200
	Hydrogen bonded	3500-3200
	Carboxylic acid	3400-2500
N-H	Primary and secondary amine and amide	3500-3100
C-N	Amine	1350-1000
C=N	Imine and oxime	1690-1640
C≡N	Nitrile	2260-2240
N=O	Nitro (R-NO ₂)	1600-1500, 1400-1300
S=O	Sulfoxide	1050
	Sulfate, sulfoamide	1200-1140



Characteristic bond stretching frequencies of anionic species

Anion	Wavenumber (cm ⁻¹)
SO ₄ ²⁻	1100-1200 (ν _{as})
ClO ₄ ⁻	1050-1170 (ν _{as})
NO ₃ ⁻	1370 (ν _{as})
CN ⁻	2089
SCN ⁻	2053 (νC-N), 748 (νC-S)
N ₃ ⁻	2042 (ν _{as}), 1343 (ν _s)
CNO ⁻	2052 (νC-N), 1057 (νN-O)

Number of CO stretching bands in the IR spectra of metal carbonyl complexes



Complex	Number of bands
$M(CO)_6$	1
$M(CO)_5X$	3
<i>cis</i> - $M(CO)_4X_2$	4
<i>trans</i> - $M(CO)_4X_2$	1
<i>fac</i> - $M(CO)_3X_3$	2
<i>mer</i> - $M(CO)_3X_3$	3
<i>fac</i> - $M(CO)_3X_2Y$	3
<i>cis</i> - $M(CO)_2X_4$	2
<i>trans</i> - $M(CO)_2X_4$	1



Periodic table

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
Lanthanides		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97		
Actinides		90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

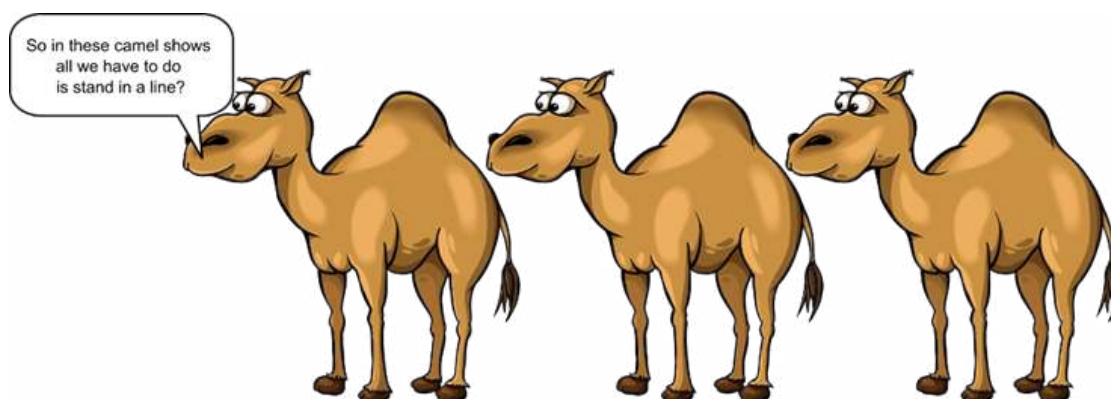


1. Stereocamelstry



A nighttime camel show in the UAE

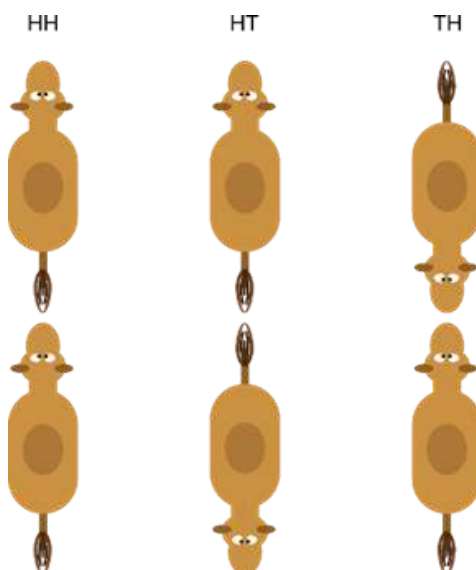
The UAE is well known for its camel shows, where camels stand in a line one after another and don't really do anything else. This arrangement of camels is called a train of camels, or a caravan of camels, and the camels are tied head to tail. This is the most convenient way of arranging camels when moving across the desert.



For this problem we shall approximate a normal camel as having a plane of symmetry along its body; its left side is the same as its right side. However, the two ends of a camel are different; a camel has a head end (H) and a tail end (T).



Colin was trying to tie lots of camels up into trains of camels that were two camels long, but was a bit forgetful and didn't think to look at which way around the camels were when he was tying them up. This resulted in three different arrangements of camels in the train being possible.



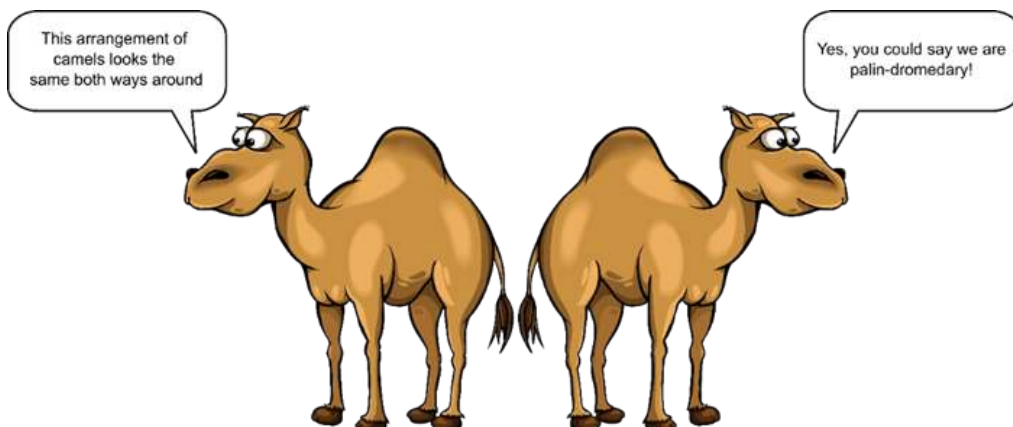
The three arrangements possible when viewed from overhead are shown above. We could call these three arrangements HH, HT, and TH respectively, based on whether the head or the tail of the camel comes first as we look from top to bottom. We might at first think that there is a fourth possible arrangement of camels (TT). However, this arrangement is not unique. If we were to view the TT arrangement from the other end, it is the same as HH.

This question requires you to draw various arrangements of camels. If your artistic skills have deserted you somewhat, then you may approximate a camel to something simpler in your drawings such as an arrow. It is important to remember though that camels are three dimensional objects.

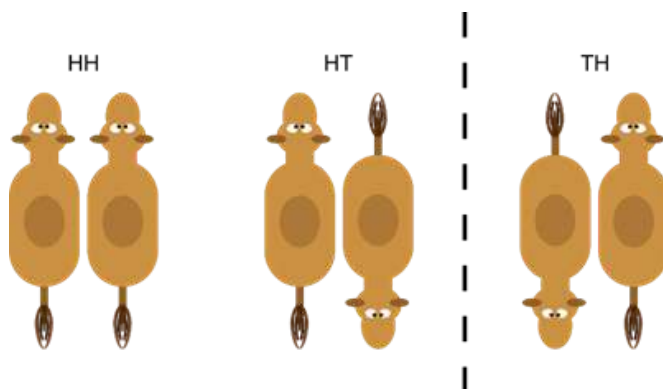


(a) **Draw** all possible arrangements of camels in a camel train that is three camels long.

(b) **Draw** all possible arrangements of camels in a camel train that is four camels long.



When camels are tied up for the night, they are sometimes arranged side by side. Let's first consider a parking arrangement where two camels are side by side. Again, Colin was a bit forgetful and didn't pay attention to which way round he was tying the camels. There are three possible side by side arrangements of two camels.



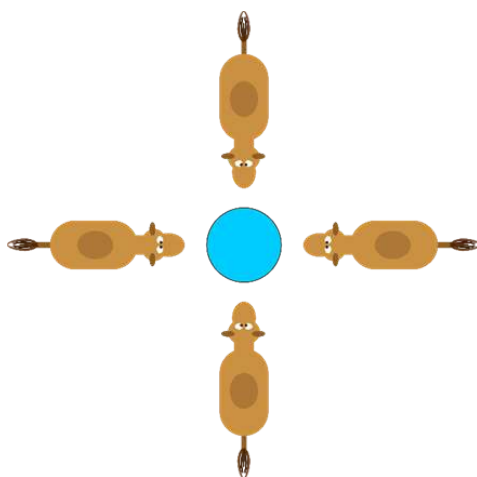
When viewed from overhead, and described going left to right, we can call these arrangements HH, HT, and TH respectively. Again, we might think there is a fourth possible arrangement of camels (TT), but this is the same as HH if viewed from the other side. The HT and TH arrangements are also interesting, as they are chiral arrangements of camels. Even though an individual camel is achiral, these two arrangements of camels are chiral overall, and they are enantiomers of each other.

(c) **Draw** all possible arrangements of camels when three camels are tied side by side, indicating which arrangements are achiral and which arrangements are chiral.



(d) **Draw** all possible arrangements of camels when four camels are tied side by side, indicating which arrangements are achiral and which arrangements are chiral.

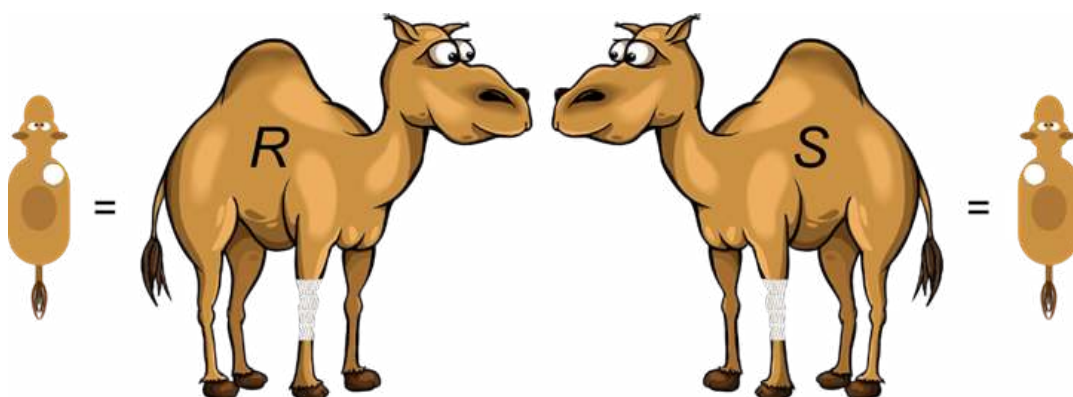
Although camels are famous for going for long periods without water, they do sometimes need to drink. A particular well has space for four camels to stand around it and drink water. To do this, the camels should be arranged around the well as shown.



However, Colin was forgetful again and did not pay attention to which was the head end, and which was the tail end, when tying them up.

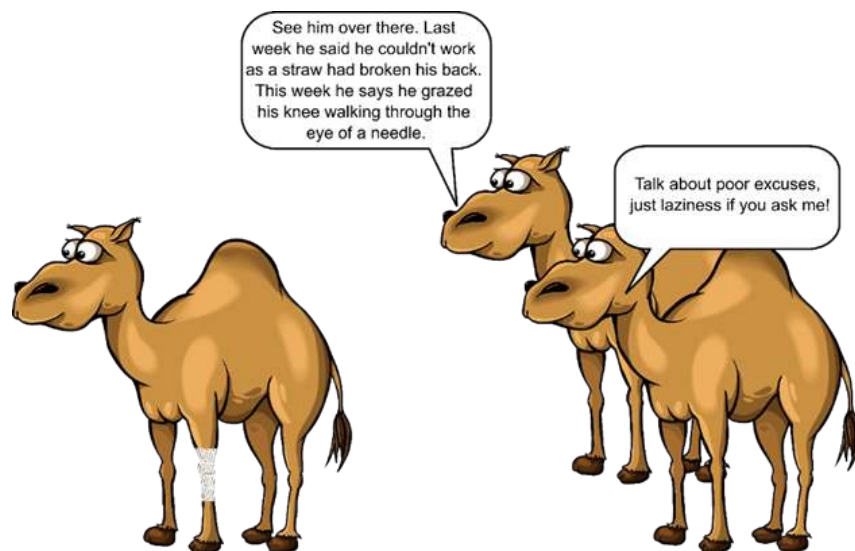
(e) **Draw** all possible arrangements of camels around the well, indicating which arrangements are achiral and which arrangements are chiral.

Carrying people across the desert is an arduous task for camels. Camels bend their front legs to sit down when carrying a rider and sometimes this leads to them injuring a leg. An individual camel who has injured one leg is no longer achiral and becomes a chiral camel. We will call chiral camels who have injured their front right leg as *R* camels and camels who have injured their front left leg as *S* camels.

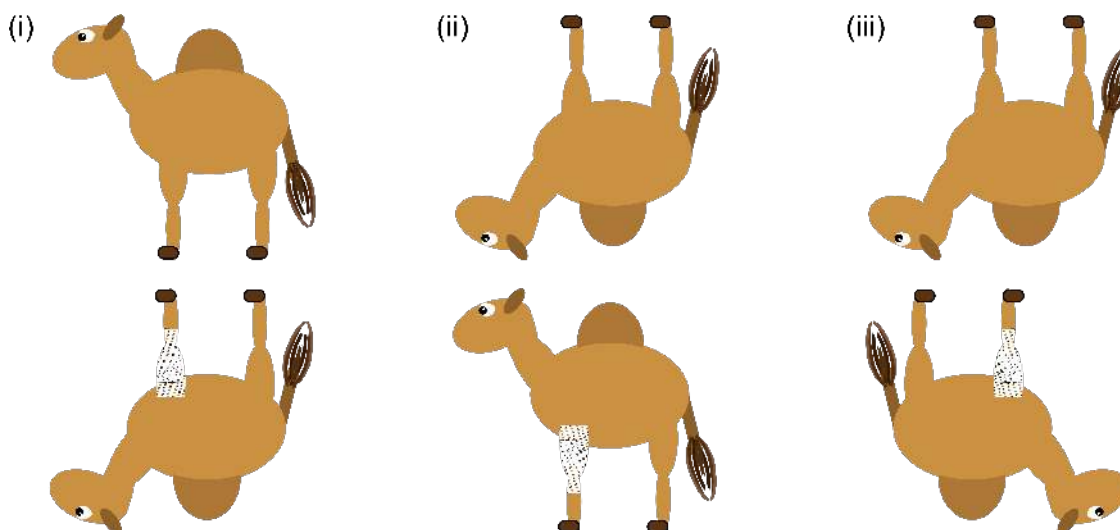




(f) **Draw** all possible arrangements of camels when two chiral camels are tied side by side, indicating which arrangements are achiral and which arrangements are chiral. Assume camels were picked randomly from a herd containing both *R* and *S* camels and then were parked randomly with no attention paid to which way around they were parked.



Fortunately, the UAE have just opened a Care Centre for Chiral Camels. To maximise efficiency, Carol the surgeon operates on two camels at once. The camels are lying down during their operation and there are three possible operation layouts: (i) feet-to-feet, (ii) hump-to-hump, and (iii) feet-to-hump. Note in the cartoon below only the top leg is visible.





(g) **Draw** all possible arrangements of two chiral camels on the operating table in a feet-to-feet layout, indicating which arrangements are achiral and which arrangements are chiral. Just consider the position of the two camels relative to each other.

(h) **Draw** all possible arrangements of two chiral camels on the operating table in a hump-to-hump layout, indicating which arrangements are achiral and which arrangements are chiral. Just consider the position of the two camels relative to each other.

(i) **Draw** all possible arrangements of two chiral camels on the operating table in a feet-to-hump layout, indicating which arrangements are achiral and which arrangements are chiral. Just consider the position of the two camels relative to each other.

No camels were harmed in the making of this question.



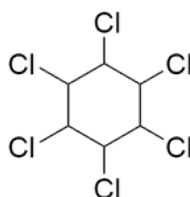
2. Mirror, mirror plane on the wall, who's the deadliest of them all?



In the fairy tale *Snow White*, the evil queen looks at her reflection in the mirror and asks, “*Mirror mirror on the wall, who is the fairest one of all?*” The queen assumes she sees her exact self in the mirror; however, this is not always true. The reflection of a chiral object in a mirror gives its enantiomer. Sadly, for us chemists, this book from 1812 does not specify whether the queen was a chiral object or not.

Some compounds are formed as mixtures of many isomers, some of which are chiral, and some are not. Different isomers often have different chemical properties including how toxic they are. This is problematic if the synthesis leads to a mixture of isomers, but not all isomers are useful.

2025 is the 200th anniversary of the discovery of one of these compounds, 1,2,3,4,5,6-hexachlorocyclohexane (**HCH**), where many isomers turned out to be very toxic.



In 1825, British scientist Michael Faraday reported the discovery of benzene, which he had extracted from products of the pyrolysis of sperm oil. Through a series of meticulous experiments, he identified the accurate mass percentage of carbon and hydrogen in benzene. However, due to the concept of “proportionals” in use in science at the time, Faraday called this molecule the “*bi-carburet of hydrogen*” as 11.44 was close to 12, which was two “proportionals” of carbon.

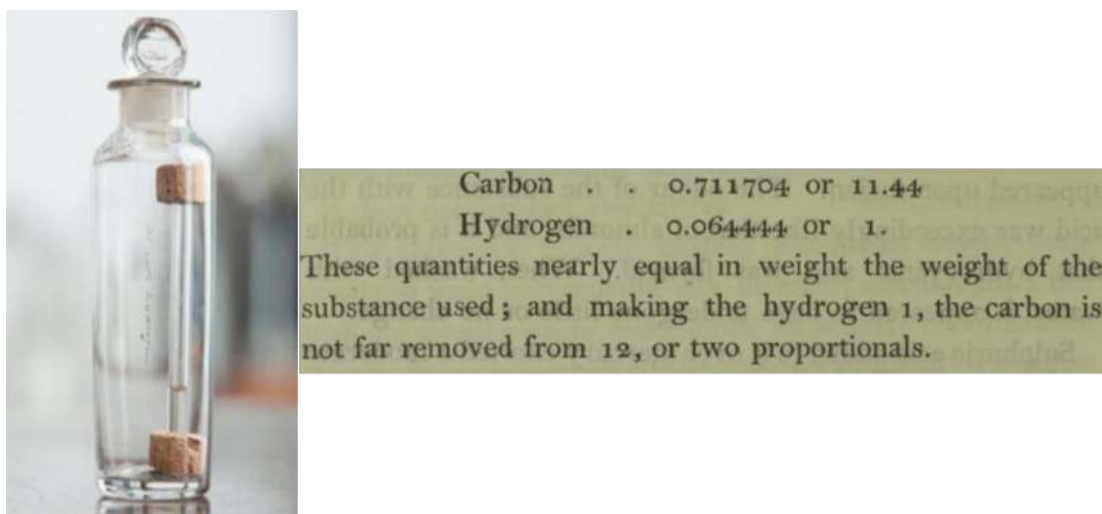


Figure 1: Left. Faraday's sample of the bi-carburet of hydrogen which is kept at the Royal Institution. Right. Faraday's determination of the mass percentages in benzene.

Faraday also reported the reaction of benzene with various other chemicals including chlorine gas.

Chlorine introduced to the substance in a retort exerted but little action until placed in sun-light, when dense fumes were formed, without the evolution of much heat; and ultimately much muriatic acid was produced, and two other substances, one a solid crystalline body, the other a dense thick fluid. It was found by further examination, that neither of these were soluble in water; that both were soluble in alcohol—the liquid readily, the solid with more difficulty. Both of them appeared to be triple compounds of chlorine, carbon, and hydrogen; but I reserve the consideration of these, and of other similar compounds, to another opportunity.

Figure 2: Faraday's description of the reaction of benzene and chlorine under sunlight.

Several different equations could be written to describe his observations, likely due to the presence of impurities in the sample. However, the "solid crystalline body" produced was the first synthesis of **HCH**. Faraday correctly deduced that this compound contained carbon, hydrogen, and chlorine, but was unable to identify it further or know that it contained a mixture of isomers.

A modern synthesis of **HCH** involves the treatment of benzene with chlorine gas under UV light. The reaction is a free-radical addition.

(a) **Write** an equation for this reaction.



HCH exists as nine stereoisomers. For the purposes of parts (b) and (c) consider the cyclohexane ring to be flat.

(b) **Draw** all the stereoisomers of **HCH**.

The nine stereoisomers of **HCH** are named with the following Greek letters.

α^+

α^-

β

γ

δ

ϵ

ζ

η

θ

(c) Using the following clues, as far as possible, **assign** the Greek letters to each of the isomers.

- The β and ϵ isomers contain centres of inversion.
- The ζ isomer is not an epimer of the α^+ isomer.
- The θ isomer is an epimer of the η isomer.
- The γ isomer has more planes of symmetry than the δ isomer.
- The η isomer does not possess a plane of symmetry through any of the atoms.
- The + and – refer to dextrorotatory and levorotatory respectively.
- The β isomer has by far the lowest chemical reactivity.

(d) **Explain** why the β isomer has by far the lowest chemical reactivity.

Many years later, the mixture of isomers of **HCH** was found to have potent insecticidal activity. Dutch chemist Teunis van der Linden was the first to isolate and describe γ -**HCH** in 1912 and this isomer was named “lindane” after him. By 1942, it was realised that lindane (γ -**HCH**) was the isomer responsible for the potency of the insecticide and γ -**HCH** went on sale as a seed treatment in 1949 called *Mergamma A*, which contained 1% mercury and 20% lindane. The mercury was removed later for safety reasons, but lindane products remained on sale for over 50 years.

Whilst the γ -isomer of **HCH** was available in >98% purity by this point, this was achieved through purification; the synthesis of **HCH** always gave a complex mixture composed of 65-70% α -**HCH**, 7-10% β -**HCH**, 14-15% γ -**HCH**, 7% δ -**HCH**, 1-2% ϵ -**HCH**, and 1-2% of the other isomers. Once separated, the remaining isomers were dumped creating huge chemical waste problems.

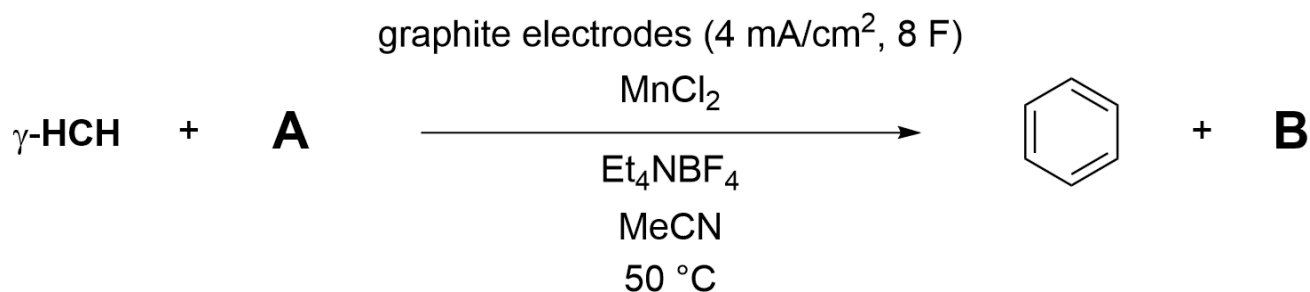


Figure 3: Mountains of the useless isomers of **HCH** which were dumped as waste in places such as Eastern Europe (left) and France (right).

(e) **Suggest** why very little of the ζ -**HCH**, η -**HCH**, and θ -**HCH** isomers are formed during synthesis.

Over time the toxicity of γ -**HCH** itself became apparent. The γ -isomer is now classified by the World Health Organisation as acutely toxic. Prolonged exposure leads to various symptoms including headaches, dizziness, seizures, convulsions, and even death in extreme cases. An international ban on the use of γ -**HCH** in agriculture came into effect in 2009. The α -**HCH** and β -**HCH** isomers, which were dumped as chemical waste, proved to be even more toxic. All isomers show long term persistence in the environment and hence still cause problems today.

In 2021, a research team led by Swiss chemist Bill Morandi developed a new way to clean up **HCH** waste through electrolysis. His reaction reverses the reaction performed two centuries earlier by Faraday, as γ -**HCH** is converted back to benzene. However, rather than produce toxic chlorine gas, the chlorine atoms are transferred to another readily available non-cyclic alkene starting material **A**, giving chloroalkane **B** as a by-product. This makes the transformation overall redox neutral. This process is highly synthetically useful as it removes toxic **HCH** waste and produces two valuable chemical products: benzene and chloroalkane **B**.



The mass spectrum of compound **B** gave the following ions: m/z 238.125 (100.0%); 239.128 (13.0%); 240.122 (63.9%); 241.125 (8.3%); 242.119 (10.2%); 243.122 (1.3%). Percentages listed show the relative amounts with the most intense peak set at 100%.

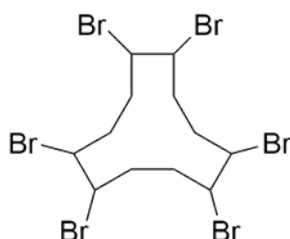


(f) **Determine** the formula for **B**.

Compound **B** is produced as a racemic mixture of two enantiomers. As this process was designed to potentially be run on a large scale, compound **A** was chosen to be as simple/cheap as possible.

(g) **Propose** structures for compounds **A** and **B**.

The compound 1,2,5,6,9,10-hexabromocyclododecane (**HBCD**) has a lot of structural similarity to **HCH**. It also exists as multiple different stereoisomers; many of which are produced during its synthesis.



Dubai is famous for skyscrapers and high-rise buildings. Although not an issue in the UAE, many tall buildings in colder climates use polystyrene foam for thermal insulation. This insulation is very flammable, and due to the fire risks in tall buildings, flame retardants are put on this polystyrene foam. **HBCD** is used as one such flame retardant.

(h) **Draw** all the stereoisomers of **HBCD**, indicating which ones are chiral and which ones are achiral.

HBCD is also now known to have significant toxicity problems and be long lived in the environment. Assessing overall toxicity is complicated because the different isomers have different toxicities and break down at different rates.

Unlike **HCH**, the **HBCD** commercial product is used as a mixture of isomers. **HBCD** is produced from the bromination of cyclododeca-1,5,9-triene. Four isomers of cyclododeca-1,5,9-triene are possible: (i) all-*cis*; (ii) *cis,cis,trans*; (iii) *cis,trans,trans*; and (iv) all-*trans*.

(i) Assuming the standard mechanism of alkene bromination, **determine** which **HBCD** isomers are produced from each of the four possible starting materials.

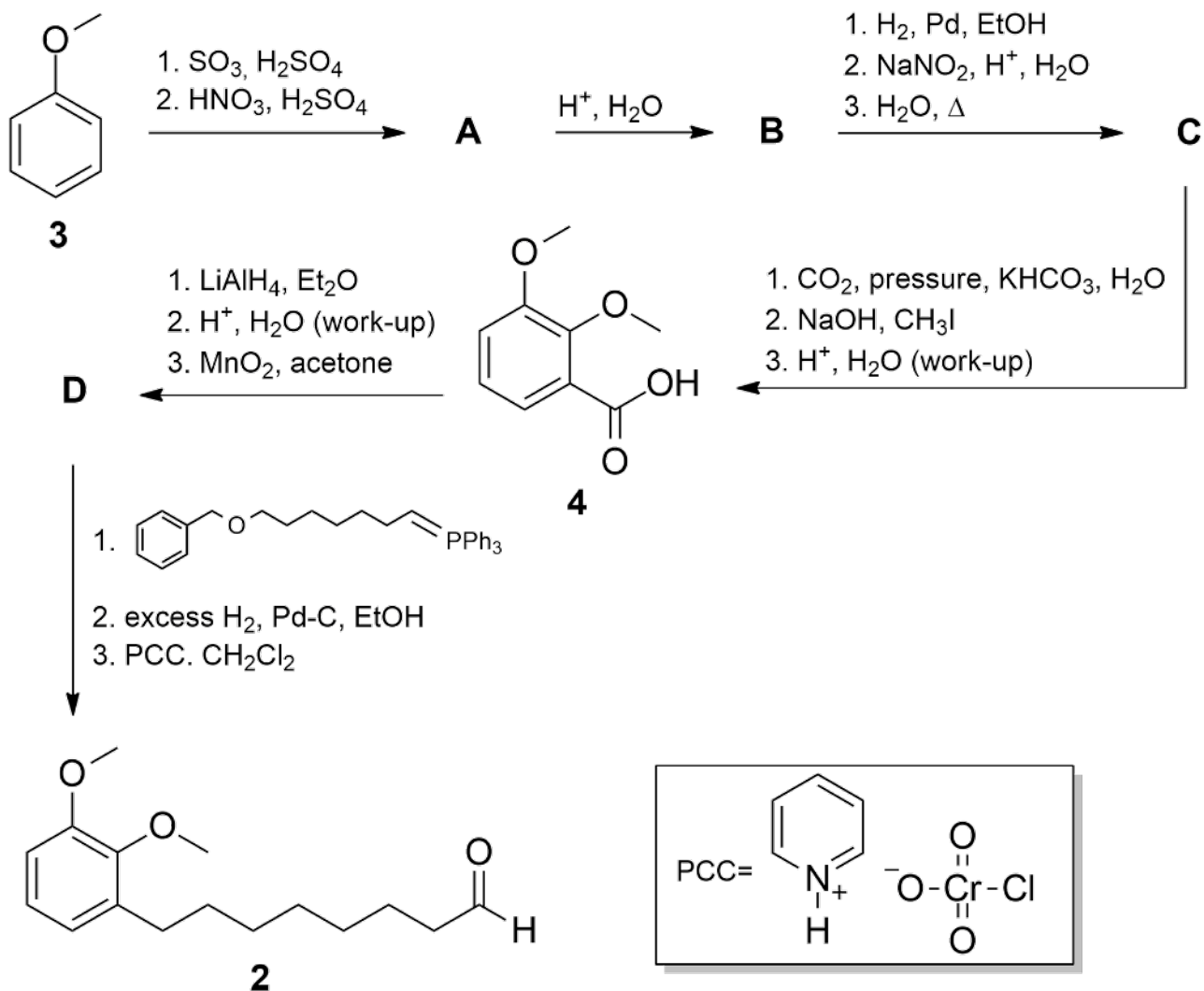
(j) Given the commercial **HBCD** product is quoted as containing “three major diastereoisomers”, **is it possible** to determine which isomer of cyclododeca-1,5,9-triene is used as the starting material for the commercial synthesis?



Urushiols are compounds that cause skin irritation. They are the active compounds in gypsum and poison oak that cause skin rash. Some chemical modifications of Urushiols I and II are shown below.



The synthesis of compound **2** is shown below.

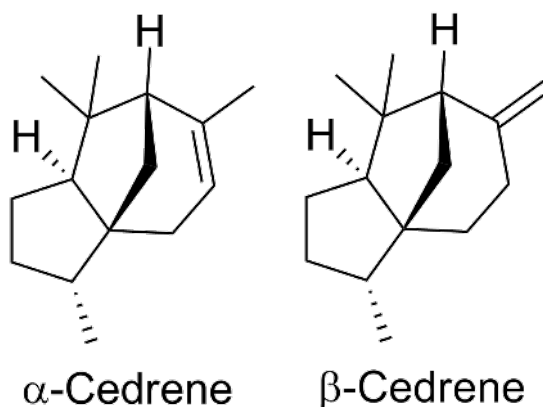


(b) **Draw** the structures of **A-D** that are obtained after work-up.



4. Cedrene

Sesquiterpenes are a class of organic structures that contain three isoprene units and often have the molecular formula $C_{15}H_{24}$. Cedrene is one such compound that is found in the essential oil of cedar. There are two types of cedrene, α and β , which differ in the position of the double bond.



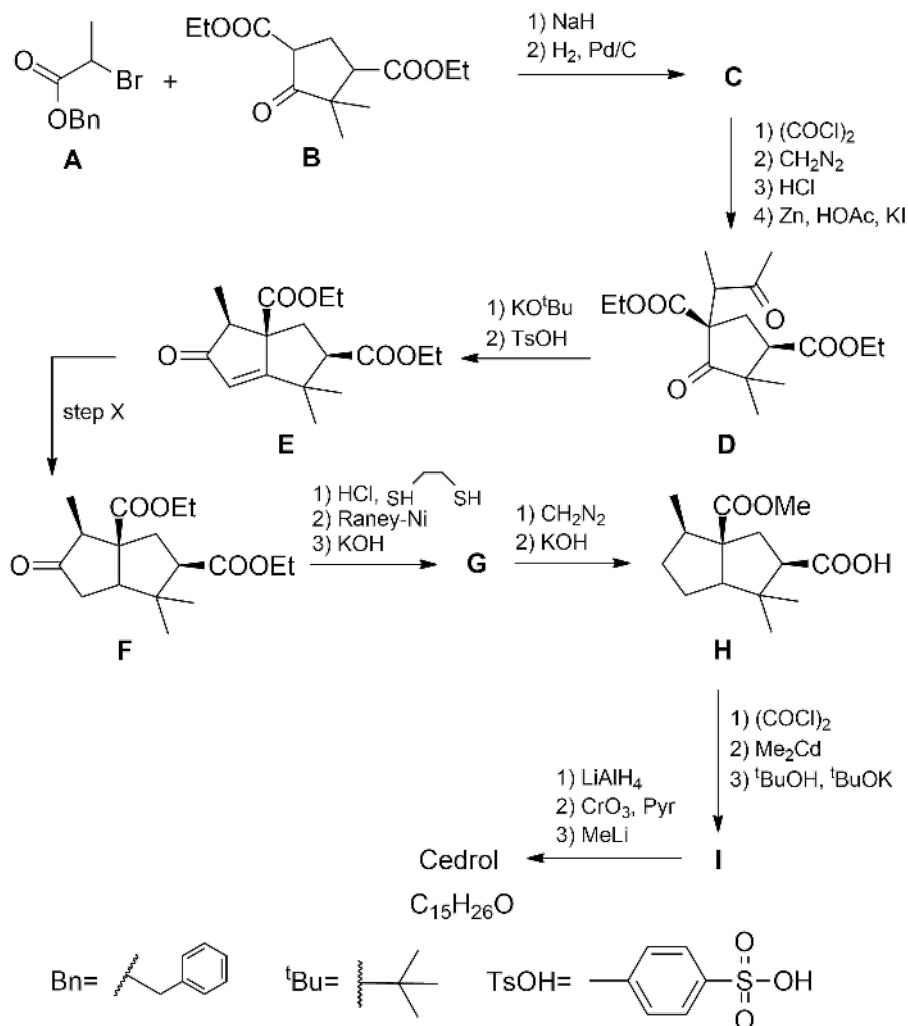
(a) **Circle** the stereocentres in α -cedrene and **assign** them as *R* or *S*.

There are various ways to synthesise cedrene. In this exercise we look at two of these methods.

In 1955 Stork *et al.* used an eight step synthesis to make cedrol, a precursor to cedrene. It is possible to convert cedrol to cedrene by adding a sulfate salt. The synthesis of cedrene starts from compounds **A** and **B**.

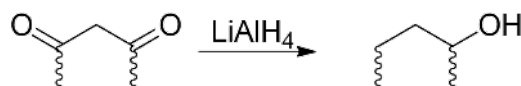


Method 1: Synthesis of α -cedrene by Stork et al. (1955)



Additional hints:

- Pyr=pyridine;
- $(\text{COCl})_2$ works similar to SOCl_2 ;
- CrO_3 , Pyr converts alcohols to ketones;
- Organocadmium reagents work similar to Grignard reagents;
- Cedrol can be converted to cedrene via an elimination reaction in which water is removed;
- LiAlH_4 performs a reaction similar to the one shown below.





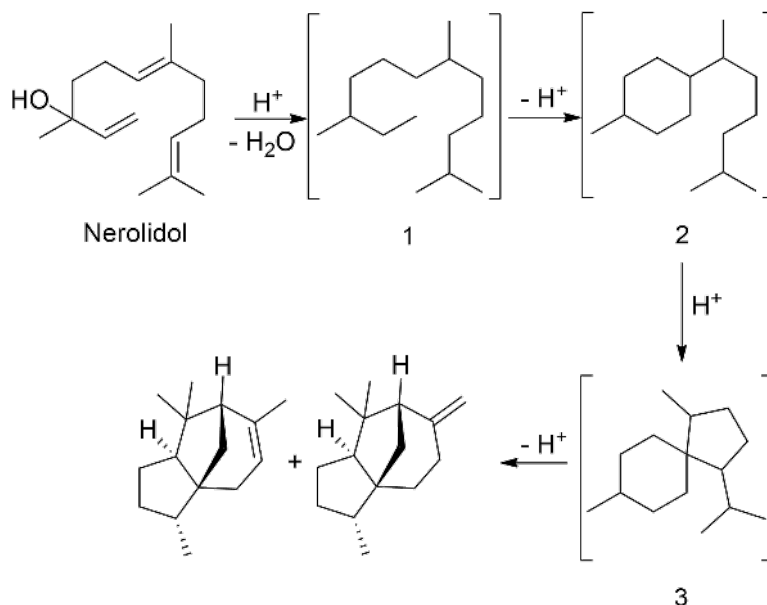
(b) **Draw** the structures of **C**, **G**, **I**, and **cedrol** that are obtained after work-up. You do not need to show stereochemistry.

(c) **Tick** which reagent(s) would be suitable for step X.

☐ Li, NH₃ ☐ LiAlH₄ ☐ H₂, Pd/C ☐ HNO₃ ☐ H₂SO₄

Method 2: Cyclisation of nerolidol

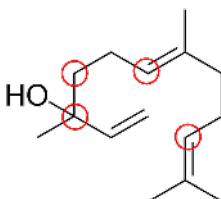
It is also possible to isomerise the structure of nerolidol to both α -, and β -cedrene by adding acid. This will remove the alcohol group and start a cyclisation reaction. The conversion takes place via multiple intermediate structures. Incomplete structures of three of these intermediates are shown.



Intermediates **1** and **3** are charged. Intermediate **2** is neutral.

(d) **Complete** the structure of intermediates **1**, **2**, and **3** by adding double bonds and charges in the correct places.

Four carbon atoms are circled in nerolidol. Through understanding the mechanism we can determine where these four carbon atoms end up in cedrine.





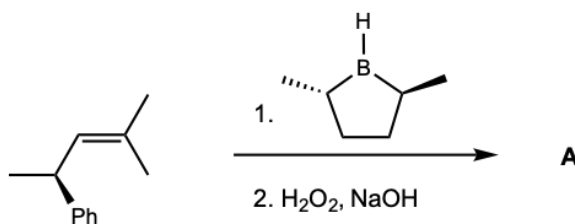
(e) **Circle** the four corresponding carbon atoms in cedrene (α or β) which were circled in nerolidol.



5. Stereochemical models

Stereochemistry is abundant in the natural world, with most molecular building blocks of life being chiral. While the origin of homochirality is still a subject of much debate, there is no doubt about the importance of stereochemistry in biological systems. The famous thalidomide tragedy occurred due to one stereoisomer having therapeutic effects while the other stereoisomer was teratogenic. Since then, synthetic chemists have focussed efforts on developing methods to make molecules in a stereoselective way. In this question, we will explore different aspects of stereochemical control.

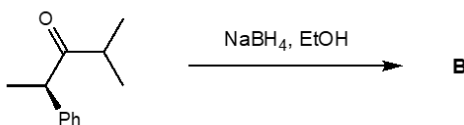
One of the simplest ways to perform a stereoselective reaction is through the use of a chiral reagent.



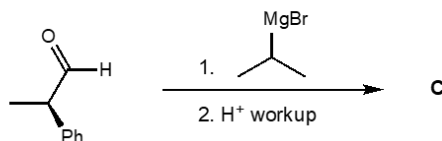
(a) By considering the transition state for the hydroboration reaction across the double bond, **draw** the structure of the major stereoisomer **A**.

Instead of using a chiral reagent, the presence of a stereocentre nearby can also help to control the stereochemical outcome of a reaction. Imagine you want to synthesise product **A** starting from a carbonyl group. You could come up with two methods to do this (Reaction **B** and Reaction **C**).

Reaction **B**:



Reaction **C**:



The stereochemical outcome of the reactions can be predicted using the Felkin-Anh model.



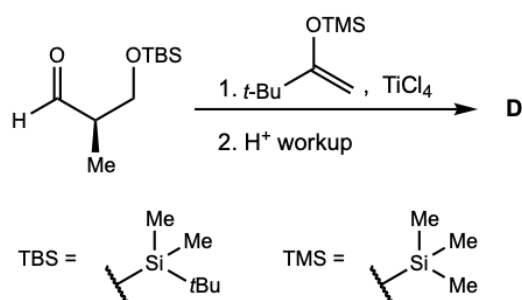
(b) For each reaction, **draw** a Newman projection showing the ideal approach of the nucleophile. Use the labels =O, -H, -Ph, -Me and -*i*Pr. Show the structure of the nucleophile in full.

(c) **Draw** the structures of compounds **B** and **C**, indicating the stereochemistry clearly.

(d) **Which** reaction should you use to synthesise product **A**?

- ☐ **B** ☐ **C** ☐ Either **B** or **C** ☐ Neither **B** nor **C**

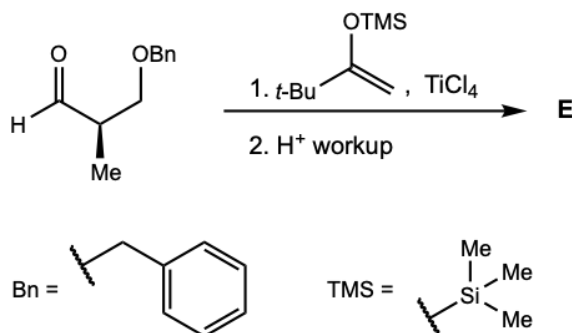
Often, the stereochemical outcome can be influenced by a small change in the reagent. Let's predict the stereoselectivity of the following reaction using the Felkin-Anh model:



(e) **Draw** a Newman projection showing the ideal approach of the nucleophile. Use the labels =O, -H, -Me, -CH₂OTBS and Nu.

(f) **Draw** the structure of compound **D**, indicating the stereochemistry clearly.

The stereochemical outcome of the reaction can be changed by using a different alcohol protecting group.



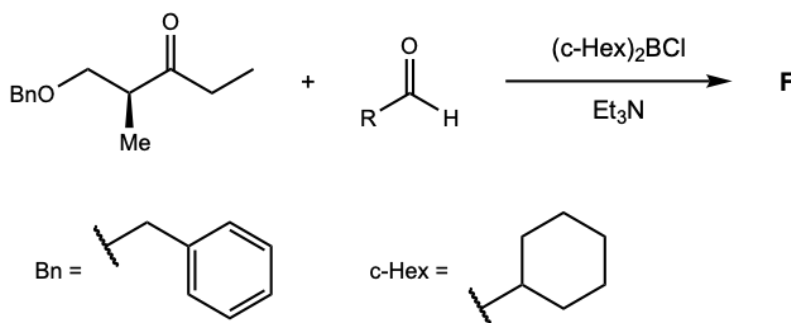


(g) **Draw** a diagram of the transition state in this reaction. *Hint:* It involves the formation of a six-membered ring adopting a half-chair conformation.

(h) **Draw** the structure of compound **E**, indicating the stereochemistry clearly.

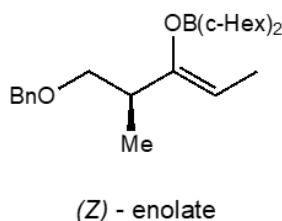
(i) **Why** does the Felkin-Anh model not predict the correct stereoisomer in this example?

Six-membered rings are highly favoured thermodynamically, and many organic reactions go through transition states that involve six-membered rings. One example is the aldol reaction, which goes through a six-membered ring Zimmerman-Traxler transition state.

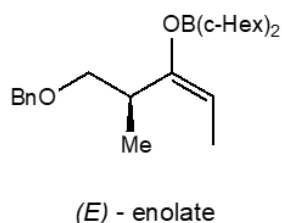


(j) **Determine** the geometry of the boron enolate formed.

a.



b.

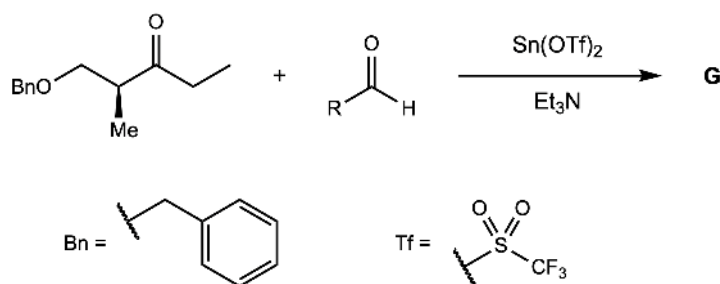




(k) Using the Zimmerman-Traxler model, **draw** the arrangement of the reactants as they come together to form the six-membered ring transition state in the reaction to form **F**. *Hint:* The Houk model predicts that stereocentre next to an alkene favours a geometry with the smallest group eclipsing the double bond. However, in this case, the smallest group should be facing the large Boron substituents to minimise steric strain.

(l) **Draw** the structure of compound **F**, indicating the stereochemistry clearly.

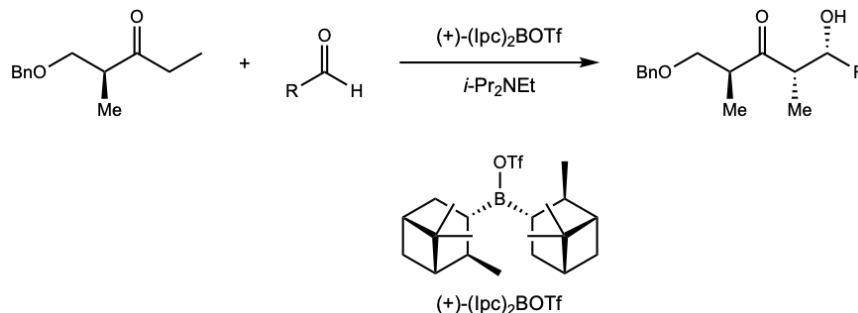
Once again, changing the reaction conditions can lead to the formation of a different stereoisomer.



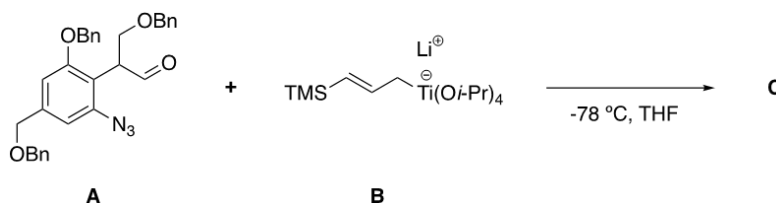
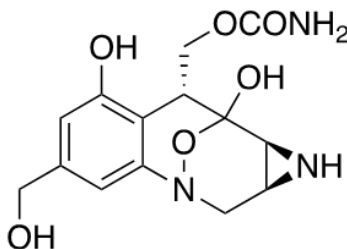
(m) Using the Zimmerman-Traxler model, **draw** the arrangement of the reactants as they come together to form the six-membered ring transition state in the reaction to form **G**. *Hint:* Carefully consider the geometry of the enolate. You should have two six-membered rings in this transition state.

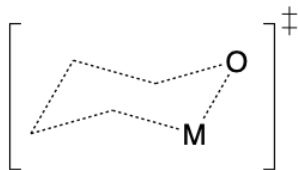
(n) **Draw** the structure of **G**, indicating the stereochemistry clearly.

In fact, using a chiral reagent, yet another stereoisomer can be formed selectively.



Rationalising the stereoselectivity of this reaction is beyond the syllabus of IChO2025 and left as a challenge to the enthusiastic student!

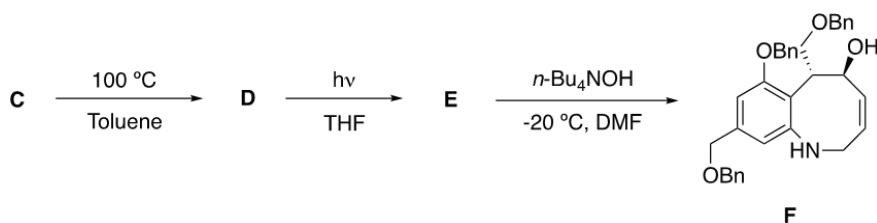




(d) **Draw** the structure of compound **C** showing all stereochemistry.

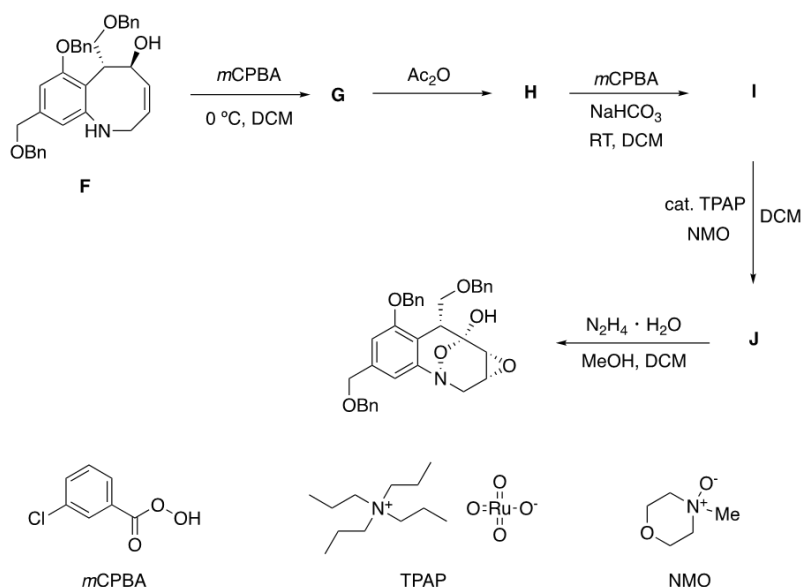
Compound **C** was further transformed into compound **D** by heating in toluene. Brief photolysis of **D** yielded **E**, which can undergo fragmentation to form **F**.

Hint: Nitrogen gas evolved during the photolysis of **D** to form **E**. **D** contained a five-membered ring while **E** contained a three-membered ring.



(e) **Draw** the structures of **D** and **E**. You do not need to indicate stereochemistry.

The next series of steps allowed the formation of the bridged bicyclic ring scaffold.



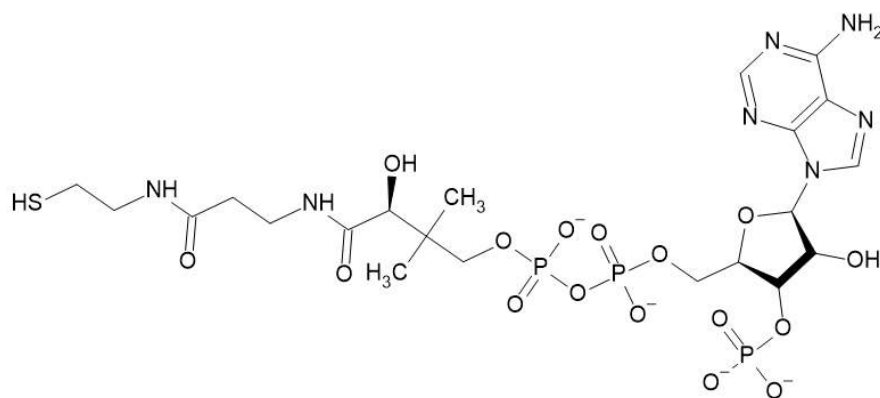
(f) **Draw** the structures of compounds **G**, **H**, **I**, and **J**. You do not need to indicate stereochemistry. *Hint:* cat. TPAP/NMO works similarly to pyridinium chlorochromate (PCC).



7. Coenzyme A and anaplerotic reactions

Glycolysis is one of the most important catabolic transformations. It affords pyruvate, which is further subjected to oxidative decarboxylation under aerobic conditions entering the tricarboxylic acid (TCA) cycle in the form of acetyl-coenzyme A (CoA), which reacts with oxaloacetate to produce citrate.

CoA is composed of three blocks, which are residues of phosphorylated ADP, pantothenic acid (vitamin B₅), and thioethanolamine:



During CoA biosynthesis, vitamin B₅ is modified from both sides.

(a) **Suggest** the canonical amino acid **X1**, from which the thioethanolamine residue originates. **Draw** the structure of the L-isomer of **X1** with stereochemical details. What is the absolute configuration (*R* or *S*) of the stereocentre?

Vitamin B₅ is produced in most bacteria by combination of pantoate and a non-canonical amino acid **X2**, which is a nearest homologue of the canonical amino acid **X3** and a structural isomer of the canonical amino acid **X4**.

(b) **Draw** the structures of **X2-X4** and pantoate.

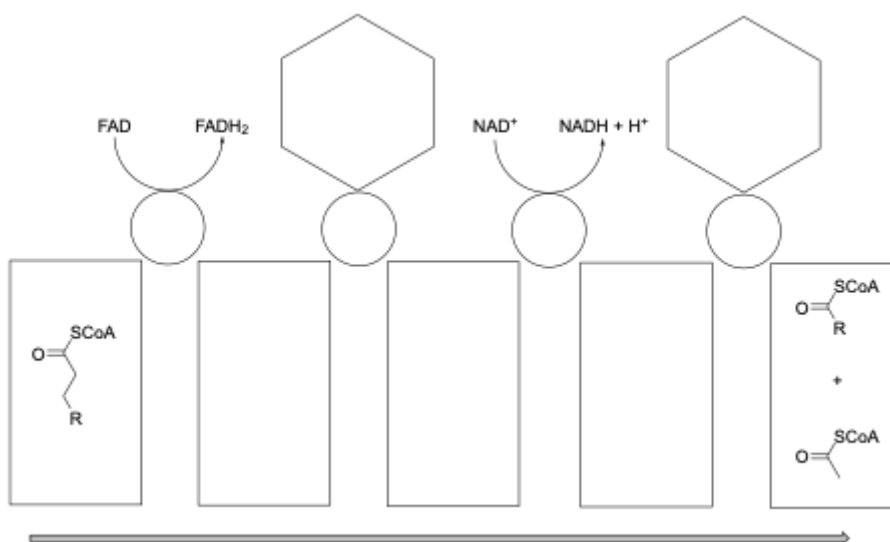
CoA is a universal carrier of acyl groups in numerous metabolic processes including degradation and biosynthesis of fatty acids. The β -oxidation of fatty acids takes place in the mitochondrial matrix through a series of four reactions collectively referred to as β -oxidation. This process is named for the successive oxidations occurring at the β -carbon, which lead to the stepwise removal of two carbon atoms from the carboxyl end of the fatty acyl-CoA molecule.



Four enzymes are involved in this process and their functions are shown in the table.

Abbreviation	Name	Function
EH	Enoyl-CoA Hydratase	Forms a β -hydroxyl carbonyl (aldol) from an α , β -unsaturated carbonyl
KT	β -ketothiolase	Cleaves the bond between the α and β -carbons in a β -keto thioester
HD	3-L-hydroxyacyl-CoA Dehydrogenase	Oxidises a hydroxyl group to a carbonyl group
AD	Acyl-CoA Dehydrogenase	Removes hydrogen atoms from the α and β positions of a carbonyl to form an α , β -unsaturated carbonyl

The process of the β -oxidation of fatty acids is shown underneath with blanks.





(c) **Fill in the circles** with the abbreviations of the enzymes needed. Each enzyme should be used once.

(d) **Draw in the hexagons** the structure(s) of the substrate(s) needed by the enzyme at each point.

(e) **Complete the rectangles** with the structures of the intermediates.

Recently CoA was found to play an important protective role in preserving a particular functional group in various enzymes from irreversible oxidation. This reaction is referred to as CoAlation.

(f) From the following functional groups, **choose** the most probable one that is being protected:

-OH -C=O -COOH -C(O)NH₂ -NH₂ NH-C(NH₂)₂⁺ -SH -S-CH₃

During the periods of rest, organisms synthesise various important molecules including storage compounds, mostly using TCA cycle intermediates as starting substrates, thus depleting the pool of cycle intermediates. As a result, glycolytic overproduction of pyruvate and phosphoenolpyruvate as well as that of acetyl-CoA is observed when energy is required again. This happens because of a diminished concentration of oxaloacetate, which slows down the initial reaction of the TCA cycle.

Most organisms can overcome this potentially dangerous situation due to four different reactions catalysed by enzymes E₁-E₄ belonging to three different classes.

Enzymes catalyse diverse reactions and can be grouped into six classes:

i) Oxidoreductases – Oxidation/reduction reactions.

ii) Transferases – Transfer of a methyl-, acyl-, amino- or phosphate group from one substance to another; kinases forming a subclass catalyse the transfer of phosphate group(s) from high-energy phosphorylated species to accepting substrate(s).

iii) Hydrolases – Hydrolytic formation of two products from a substrate.



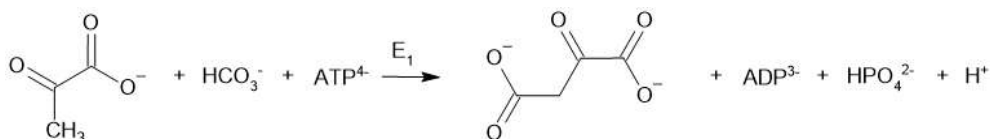
iv) Lyases – Non-hydrolytic addition or removal of groups from substrates, with C-C, C-N, C-O, or C-S bonds cleavage in the latter case.

v) Isomerases – Intramolecular rearrangement.

vi) Ligases – Joining together two molecules by formation of new C-O, C-S, C-N, or C-C bonds with simultaneous breakdown of ATP.

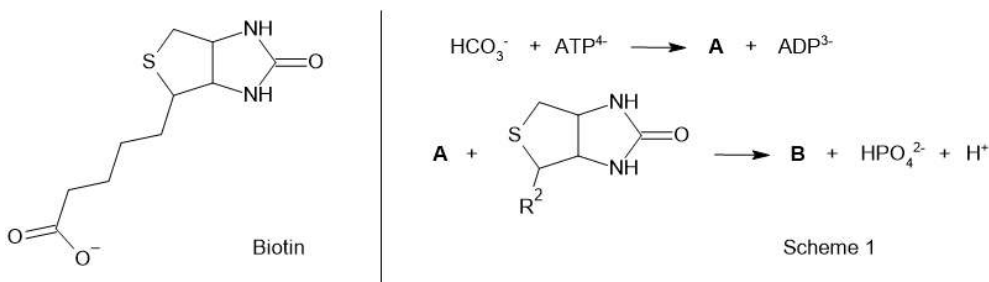
Hint: enzymes catalyse both forward and reverse reactions.

A very important reaction occurring in mammalian livers and kidneys is catalysed by E_1 :



(g) **What class** does E_1 belong to?

Biotin (see below) covalently bound to a lysine (Lys) residue is the co-factor found in the active site of E_1 . The reaction develops in two subsites, one being responsible for the biotin carboxylation (**Scheme 1**) and the other for CO_2 attachment to pyruvate.



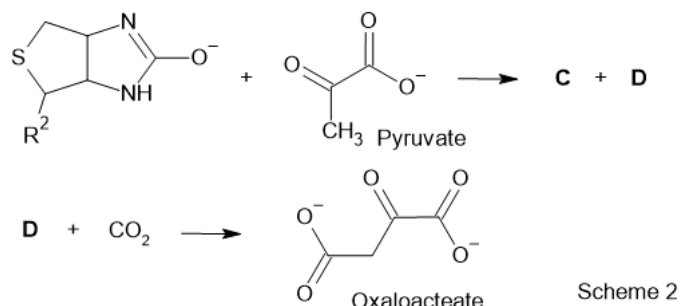
(h) **Write** the reaction between biotin and the Lys residue (show the latter as $\text{R}^1\text{-(CH}_2)_4\text{-NH}_3^+$).

(i) **Draw** the activated intermediate **A** and biotin residue with the product of addition of carbon dioxide, **B**. Show the biotin residue as in **Scheme 1**.

After being transferred to the second subunit, CO_2 leaves the biotin residue, the enol form of which further activates pyruvate by removing one of its protons to



facilitate its reaction with CO₂ (**Scheme 2**):



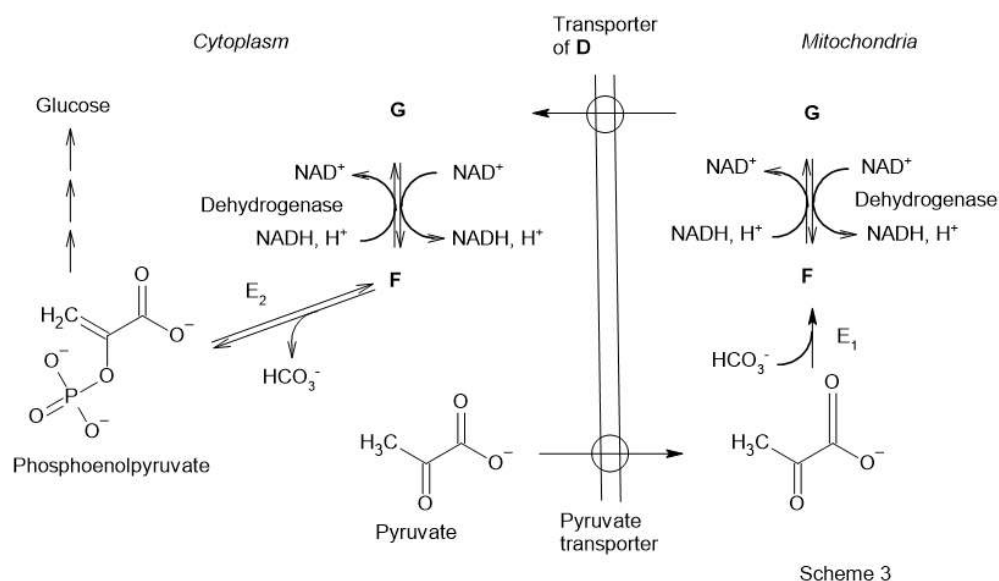
(j) **Draw** the structures of **C** and **D**.

E₂ catalyses a reversible reaction which involves (along with other reaction participants) GTP, oxaloacetate, and phosphoenolpyruvate, the latter containing nearly twice as much energy as in ATP.

(k) **Write** down the E₂ catalysed reaction.

(l) **What class** does E₂ belong to?

E₂ plays an important role in the process of gluconeogenesis where it catalyses one of the bypass steps given in **Scheme 3** (phosphorylated nucleosides and inorganic phosphate are not shown).



(m) **Draw** the structures of **F** and **G**.

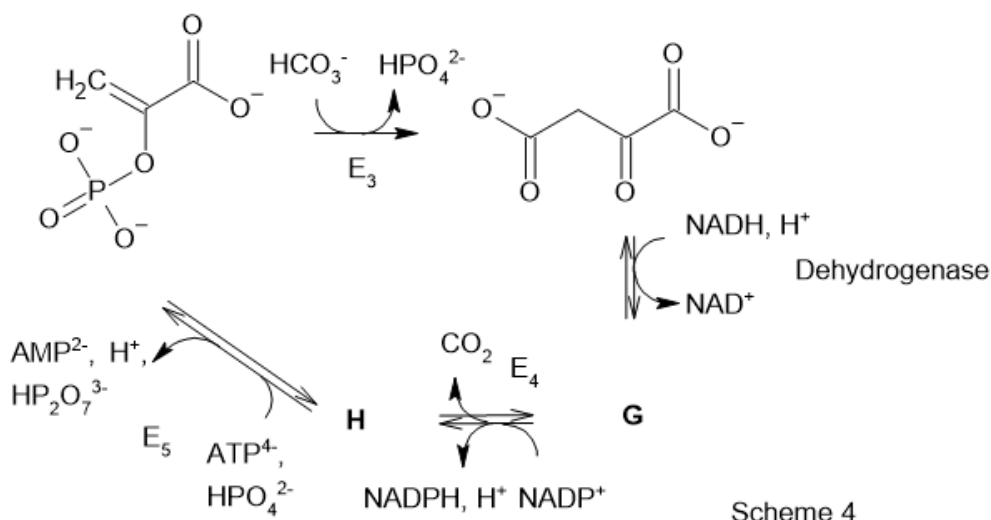


CO₂ (in the form of the hydrogencarbonate anion) is attached to pyruvate in mitochondria and is released as a result of decomposition of **F** in the cytoplasm. Studies show that this is the same species. Thus, one should not expect any label in newly formed glucose if ¹⁴CO₂ enters the carboxylation reaction instead of ¹²CO₂. However, some trace amount of labelled glucose is detected in actual experiments with ¹⁴CO₂.

(n) **Explain** the reason for this.

Hint. Some substances are intermediates of several metabolic pathways.

E₃ and E₄ are involved in the metabolic cycle found in some plants (**Scheme 4**).



(o) **Draw** the structure of **H**.

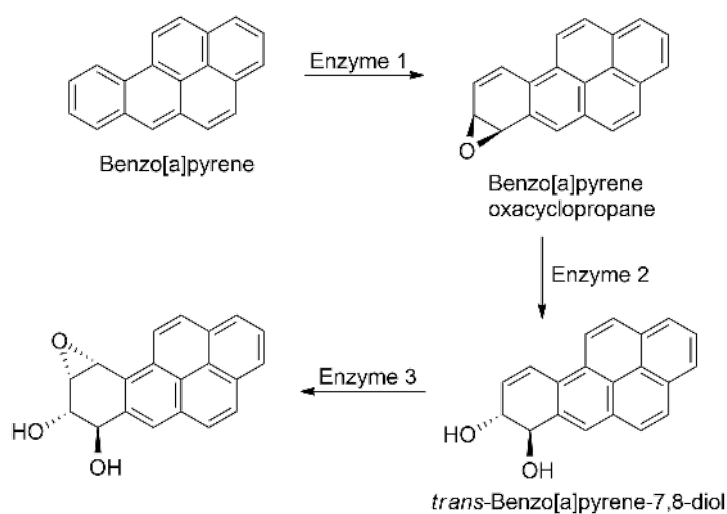
(p) **What class(es)** do E₃ and E₄ belong to?

(q) **Identify** the kinase(s) in **Scheme 4** (if any) and suggest the name of the enzyme(s).



8. Why smoking is deadly

People who smoke have an increased chance of getting lung cancer; there are multiple reasons for this. One of these reasons is the molecule benzo[a]pyrene that is released upon burning certain substances in a cigarette. When this is inhaled, it is enzymatically converted to another molecule that reacts with DNA. This disturbance of the DNA can eventually lead to cancer. The enzymatic reaction pathway is shown below.



This is an enzymatic conversion in which a reactive metabolite is formed.

(a) **Which** enzyme class do enzymes **1**, **2** and **3** belong to? **Assign** Enzyme 1, Enzyme 2, and Enzyme 3 to one of the classes given below.

- Ligase
- Isomerase
- Oxidase
- Transferase
- Hydrolase

Hint: The enzyme classes are discussed in previous problems.

The final product reacts with amine groups that are present in DNA. In this reaction the amine group attacks on the least hindered side.

(b) **Show** how the final product in the pathway above can react with this amine group. **Use** R-NH_2 to represent the amine group present in DNA.



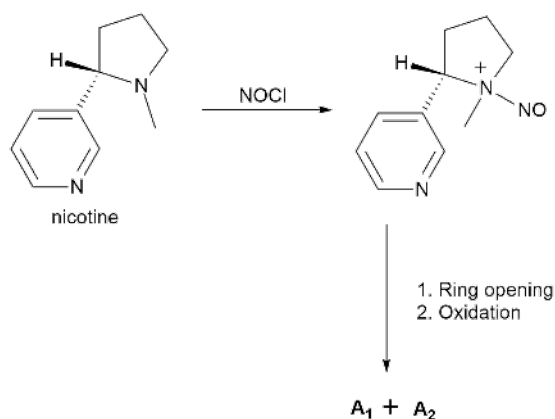
(c) **Determine** the absolute stereochemistry of all of the stereocentres in the product of the conversion above and assign them as *R* or *S*.

This mechanism also works for benzene. Therefore benzene is also carcinogenic. Toluene (methylbenzene), however, is not carcinogenic.

(d) **Draw** the structure of the product obtained by oxidation of toluene.

It has been known for years that smoking can cause cancer and now it is also known why. The number of people who smoke remains quite high. This is due to the addictive compound nicotine. This compound causes the synthesis of dopamine, which gives the feeling of joy. The absence of nicotine causes stress.

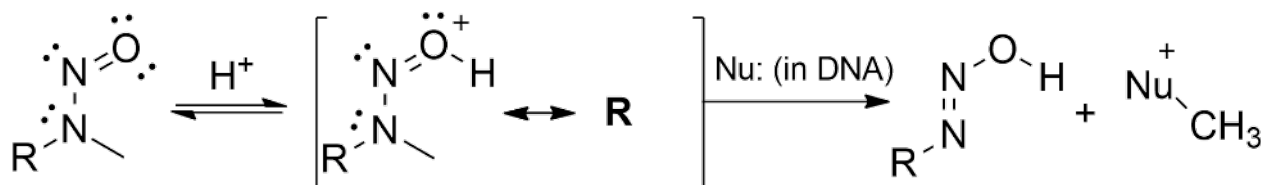
Nicotine is not only a compound that causes the above to happen. It is a known 'tumour enhancing' compound. Nicotine can also react to form two compounds that are both carcinogenic. This happens in the following way:



Both A_1 and A_2 show bands around 1700 cm^{-1} in the IR spectrum

(e) **Draw** the structural formulae of **A1** and **A2**.

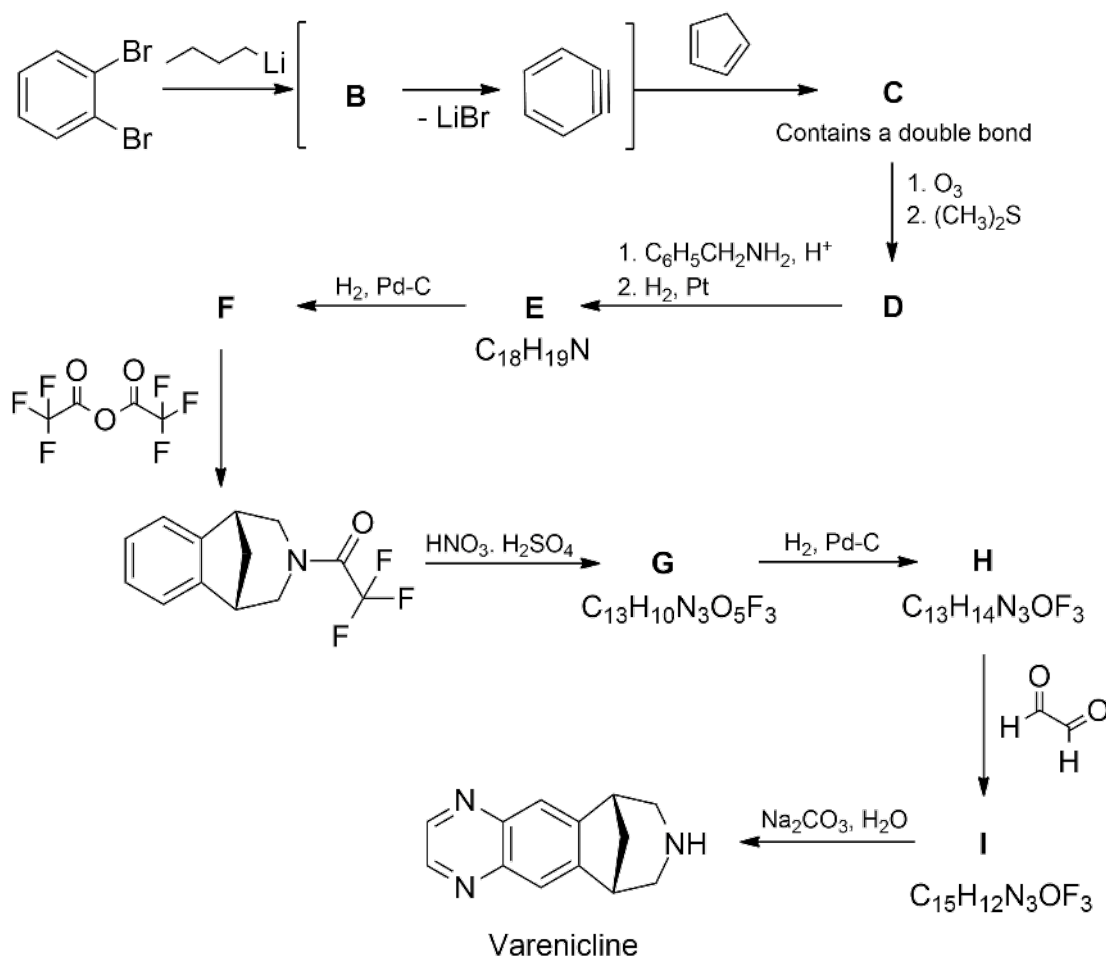
The carcinogenic effect is due to the NO group that is present in both products. Under acidic conditions, in tumour cells, the following happens:



(f) **Draw** the missing resonance form denoted "**R**" in the scheme above. All atoms in the structure follow the octet rule.



Because nicotine was used in lots of methods to quit smoking, an alternative had to be found. An alternative is the compound varenicline, that was released on the market in 2006 under the name Chantix. This compound has the same effect as nicotine, but is not as addictive. This means less dopamine is released in comparison with nicotine. This makes it easier to quit smoking. The incomplete synthesis of varenicline is shown below.



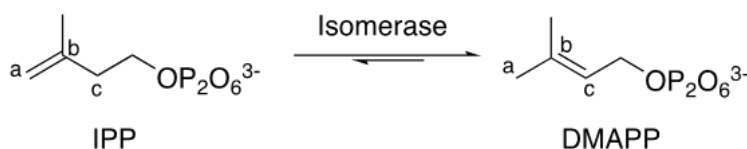
(g) **Draw** the structures of compounds **B-I**.



9. Determining the stereochemistry of enzymatic reactions

In 1975, the Nobel Prize in Chemistry was awarded to Sir John Warcup Cornforth for his work on the stereochemistry of enzyme-catalysed reactions. Enzymes are nature's chiral catalysts that perform thousands of reactions in our bodies every day, and elucidating the stereochemical result of enzymatic reactions was a huge challenge to biochemists at that time.

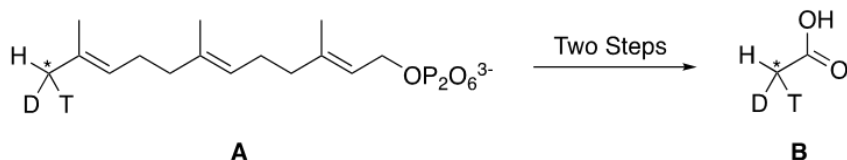
In this question, we will focus on one particular enzymatic transformation: the isomerisation of isopentenyl pyrophosphate (IPP) to dimethylallylpyrophosphate (DMAPP), by the enzyme isopentenyl pyrophosphate isomerase.



We can break down the mechanism of the reaction into two separate steps: The removal of a proton from carbon **c**, and the addition of a proton to carbon **a**. In this question, we will focus on the addition of a proton to carbon **a**.

To determine the stereochemistry of the addition of a proton to carbon **a**, one of the protons on carbon **a** in IPP was labelled with tritium (^3H , T). The isomerase reaction was carried out in D_2O , such that a deuterium (^2H , D) would be added to carbon **a**. The final product is chiral due to the modified methyl group (a CH_3 group with three different isotopes of H). In order to trap the product, another enzyme was added to catalyse the irreversible condensation of two molecules of IPP with DMAPP to form product **A**.

How can we determine the chirality of such a methyl group? To do this, an ingenious method was devised. First, chiral product **A** containing the labelled methyl group was converted to chiral acetic acid through two steps.



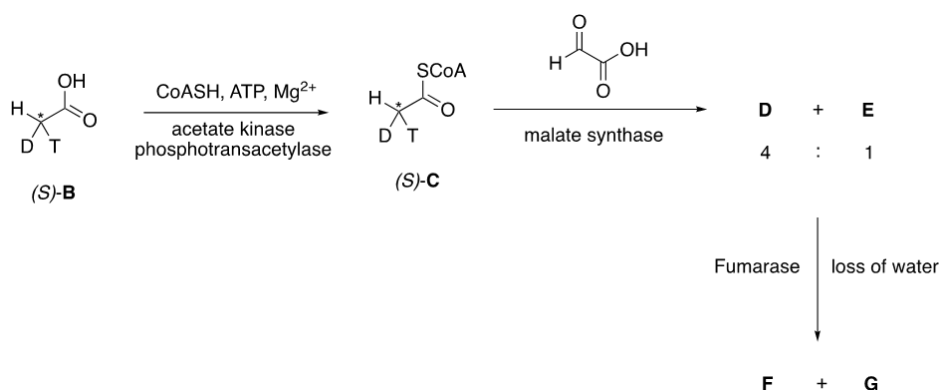
(a) **Suggest** a suitable two-step sequence of reactions that can convert chiral product **A** to chiral acetic acid **B**.



Chiral acetic acid was then subjected to a few more enzymatic transformations. For the purpose of the next part, we will consider the transformation to have been performed on the (*S*)-isomer.

(b) **Draw** the structure of (*S*)-**B**.

(*S*)-**B** was converted into chiral acetyl CoA which then reacted with glyoxylic acid to form malic acid. The second step is catalysed by malate synthase and proceeds through an attack into the glyoxylic acid (forming a new chiral centre with (*S*) configuration) with inversion of configuration at the original chiral centre. Two products are formed in a 4:1 ratio (*Hint*: kinetic isotope effect). Fumarase catalyses the anti-periplanar elimination of water from the mixture of **D** and **E** to give **F** and **G** respectively.



(c) **Draw** the structures of **D** and **E**, clearly showing the stereochemistry.

(d) **Draw** the Newman projections of the most stable conformation of both **D** and **E**.

(e) **Draw** the structures of **F** and **G**, clearly showing the stereochemistry.

The amount of tritium can be determined by measuring the radioactive activity. A ratio *Z* is defined as:

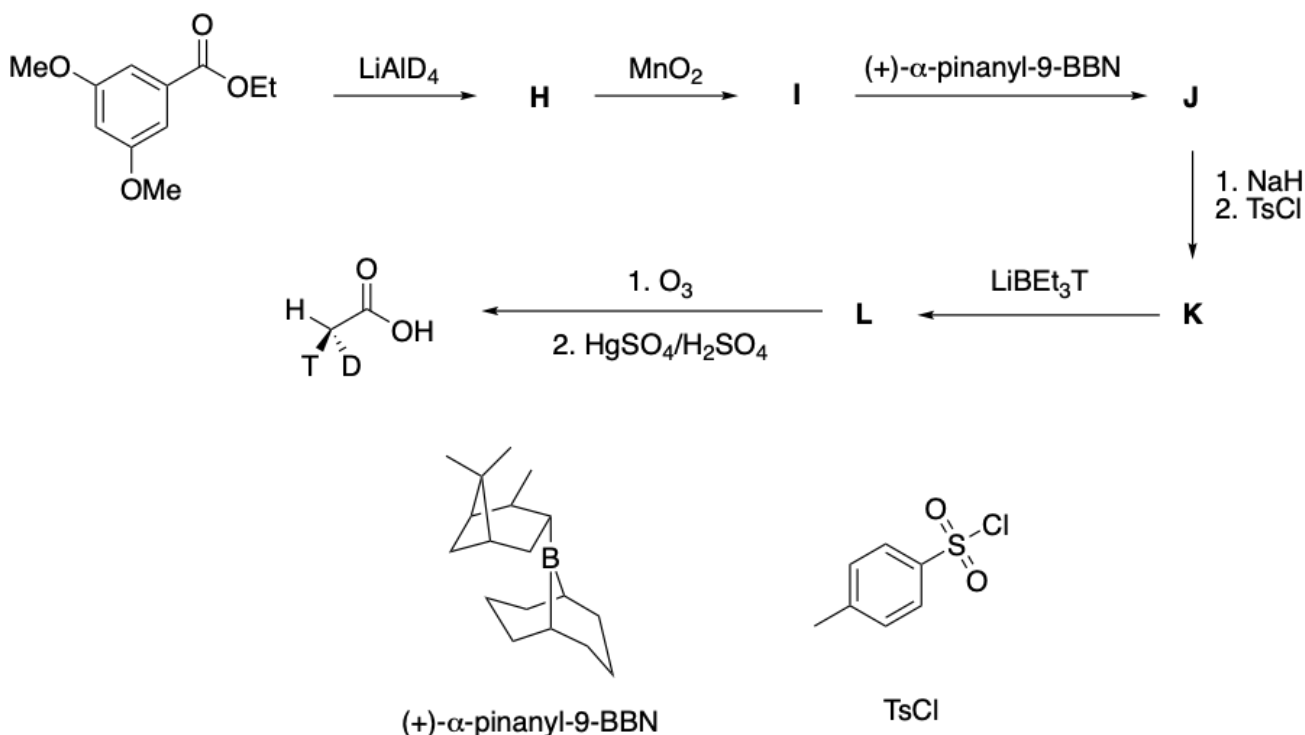
$$Z = \frac{\text{T activity after fumarase}}{\text{T activity before fumarase}}$$

(f) For (*S*)-**B**, **determine** the value of *Z*.

(g) Similarly, **determine** the value of *Z* for (*R*)-**B**.



Due to the development of this method to determine the stereochemistry of chiral acetic acid, chiral acetic acid has become a highly sought after reagent that can be used to probe stereochemistry in biological systems. Thus, new methods have been developed to synthesise chiral acetic acid. One such method is described below.



(h) **Draw** the structures of **H**, **I**, **J**, **K**, and **L**, clearly showing the stereochemistry.

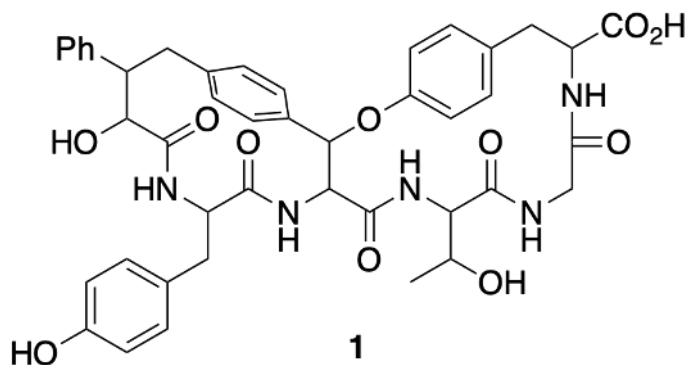
(i) **Suggest** one reagent change that will give the opposite enantiomer of the current product.



10. The synthesis and derivatisation of natural products

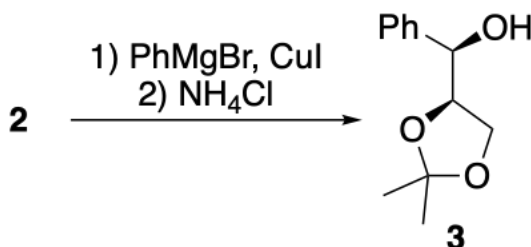
Partial synthesis of a natural product

Total syntheses of natural products are rarely performed to acquire a commercial route to a physiologically active compound of value. Rather, total syntheses are often carried out to show that they can be done or they are carried out to prove the structure of the natural product, especially its stereochemistry, when spectroscopic methods give ambiguous results. A synthesis of the latter was carried out to obtain a bicyclic hexapeptide, which had been isolated from *Aspergillus flavus*, and for which structure **1** had been assigned through complex spectroscopic studies. An Australian group from the University of Melbourne was able to synthesise structure **1**. A comparison of the synthesised molecule with the bicyclic hexapeptide isolated from *A. flavus* showed them to have different structures, meaning the stereochemistry of the natural product **1** was wrongly assigned.



(a) **Circle** all the stereocenters in structure **1**.

The total synthesis starts with the reaction presented below.



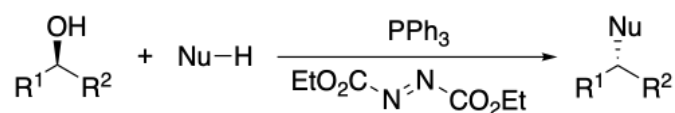
(b) **Draw** the structure of **2** including its absolute stereochemistry.



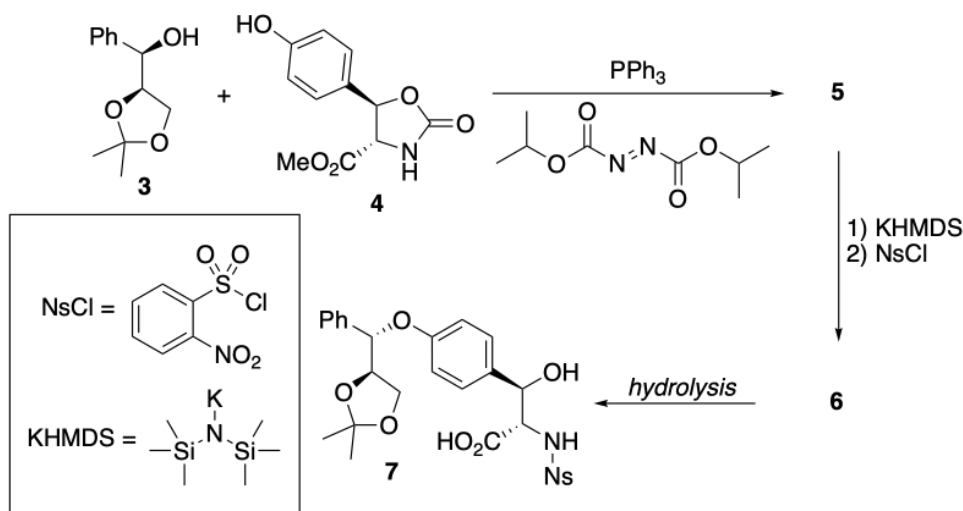
(c) **Choose** the model that can be used to predict the stereochemistry of product **3** starting from compound **2**:

- a. Felkin-Anh model without chelation
- b. Felkin-Anh model with chelation
- c. Zimmerman-Traxler without chelation
- d. Zimmerman-Traxler with chelation

The Mitsunobu reaction is a powerful transformation that helps to convert alcohols into other functionalities as presented below.



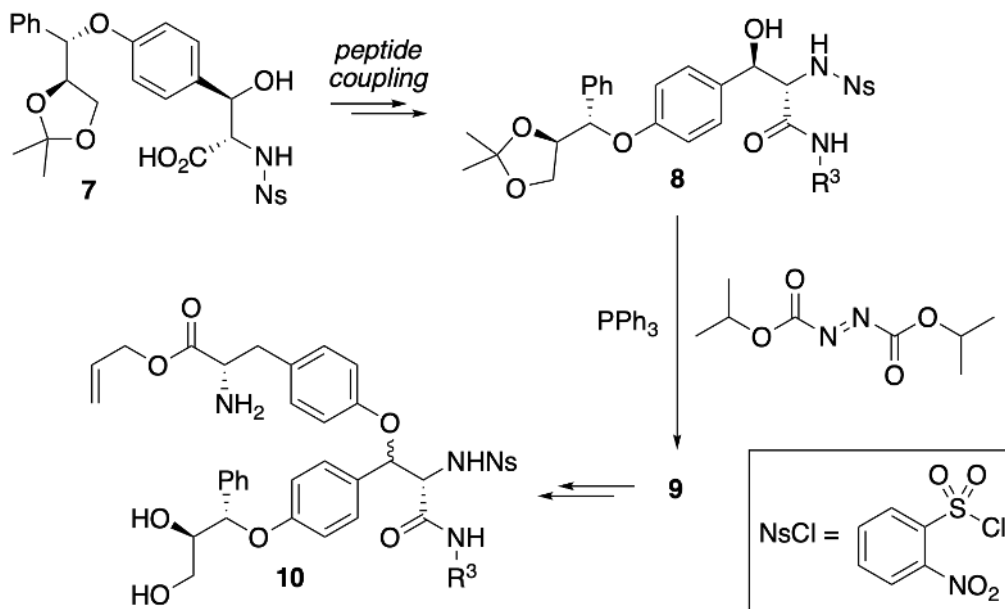
This reaction was used in the aforementioned total synthesis as demonstrated in the scheme below.



(d) **Draw** the structures of **5** and **6** including the absolute stereochemistry.



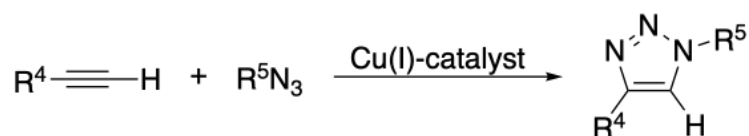
Further steps of the synthetic pathway included compounds **8-10**.



(e) **Draw** the structure of **9** including its absolute stereochemistry. *Hint: 9* is a stable compound without any charge separation.

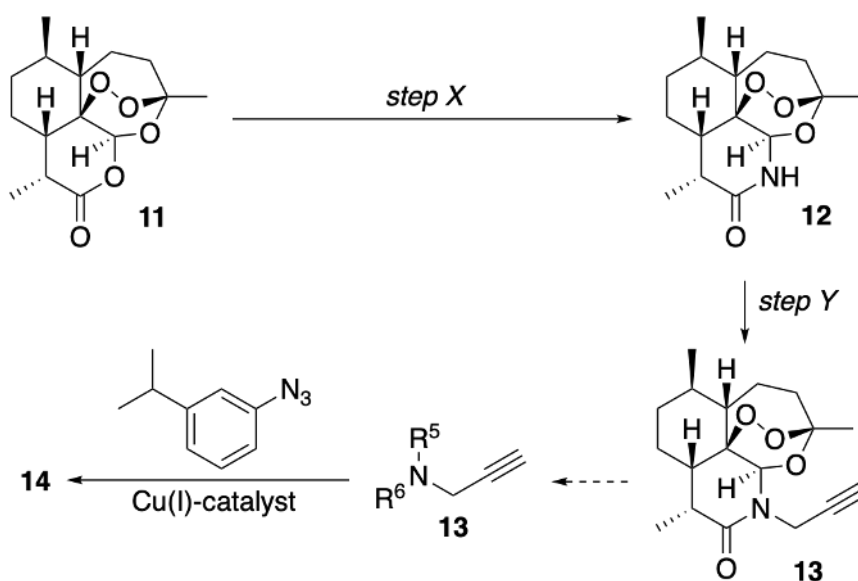
Derivatisation of a natural product

R. Huisgen (1920-2020) established the field of 1,3-dipolar cycloaddition (Huisgen cycloaddition). The azide-alkyne cycloaddition (AAC) is a reaction that gives easy access to triazoles. It is used to do various diversifications of compounds containing an alkyne fragment. K. B. Sharpless and M. Meldal developed these reactions further and realised that Cu(I) catalysis facilitated many of them (CuAAC), with the reaction field becoming part of what is now known as “click chemistry”. A general scheme for one version of CuAAC is given below.





Artemisinin **11** is a naturally occurring 1,2,4-trioxane sesquiterpene, which has exceptional antimalarial activity. In addition, several artemisinin derivatives have been found to have appreciable anticancer activity with low toxicity. In this regard, a collaboration between research groups at KU Leuven, Belgium, and NUST, Pakistan, has enabled rapid access to systems linked to triazoles such as **14**. The compounds of this series exhibited interesting biological activity and a synthesis of one of them is presented below.



(f) **Choose** the appropriate reagent(s) for steps X and Y from the table below.

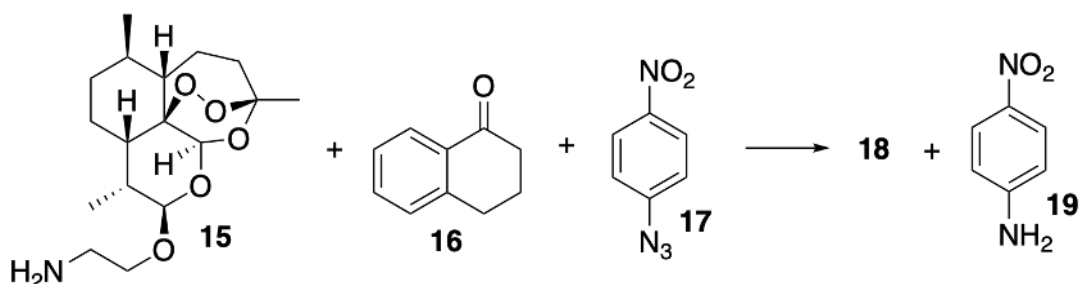
Reagent	Step	Reagent	Step
NMe_4Cl , H_2O		$Br-CH_2-CH=CH_2$, NaOH	
NH_2OH		$Br-CH_2-CH=CH-Br$, NaOH	
NH_3 (liquid)		$Br-CH_2-CH=CH-Br$, NaOH	
NH_2NH_2		$Br-CH_2-C\equiv CH$, NaOH	

(g) **Draw** the structure of compound **14**. You may use the abbreviations specified in the scheme above.



The KU Leuven group, mentioned above, devised a reaction system where triazole **18** is obtained after a reaction between artemisinin-derived amine **15**, a ketone such as **16**, and an azide-carrying reagent **17**.

The transformation is initiated by the reaction between **15** and **16**, which generates intermediate **20**. After this, compound **20** tautomerises to **21**, which has an N-H bond (unlike **20** which does not). The nitrogen atom in **20** is bonded to the same carbon atoms in the final product **18** as it was in compound **20**. The azide **17** only provides two of the three nitrogen atoms in the product, the third nitrogen atom and the rest of the reagent **17** leaves from an intermediate and forms *p*-nitroaniline (**19**) as a by-product.



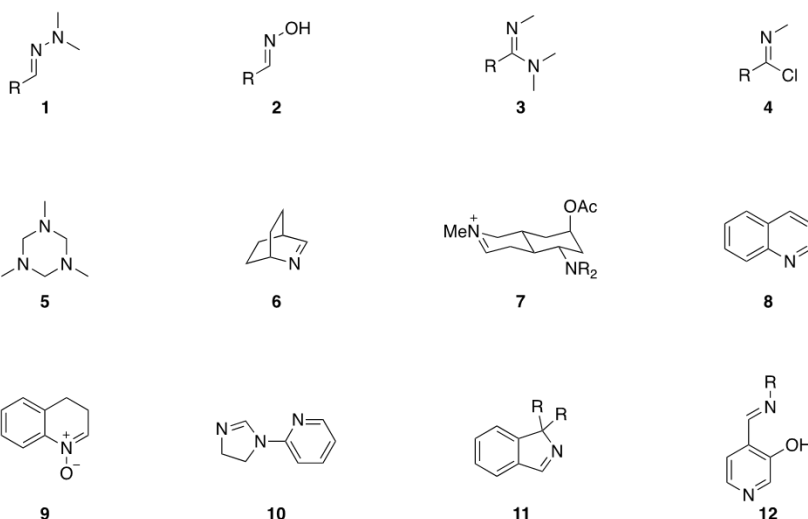
(h) **Draw** the structures of **18**, **20**, and **21**. You may use an abbreviation for **15** such as RNH₂.



11. A saga about imines

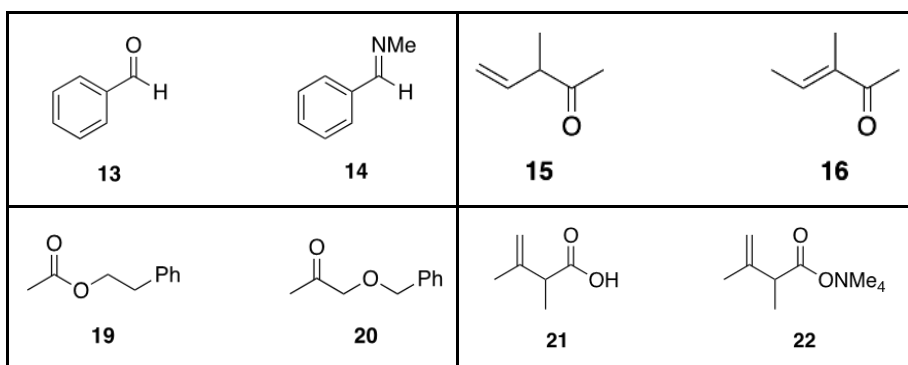
Episode IV: A new imine

An imine is a functional group in which there is a double bond between a nitrogen atom and a carbon atom and, thus, they are considered as analogues of ketones and aldehydes. As many other compounds exist with similar carbon-nitrogen bonding, other structures are often referred to incorrectly as being an “imine”. It is hard to be an imine, isn't it?



(a) From the structures above, **choose** those that have an imine functional group (assume that R is an alkyl group).

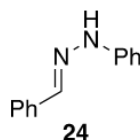
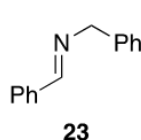
IR spectroscopy is a useful technique that allows us to differentiate between types of carbonyl compounds and related compounds.



(b) From the pairs of compounds above, **choose** the compound that shows the highest wavenumber (cm^{-1}) for the $\text{C}=\text{X}$ group ($\text{X} = \text{O}$ or NR) in its IR spectrum.



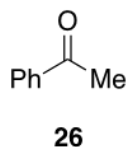
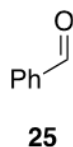
Evidently, electrophilicity of the C=N bond depends on the substitution pattern. This is illustrated with compounds **23** and **24**. One of them readily reacts with sodium borohydride at 0 °C, while the other requires lithium aluminium hydride for smooth reduction of the C=N bond.



(c) **Which** compound (**23** or **24**) **can be reduced** efficiently only with lithium aluminium hydride?

(d) **Draw** a resonance structure of that compound which shows why the carbon in the C=N bond has a lower electrophilicity.

There are many ways to synthesise imines. The simplest way is a condensation between a carbonyl compound and an amine. However, this reaction may be reversible.



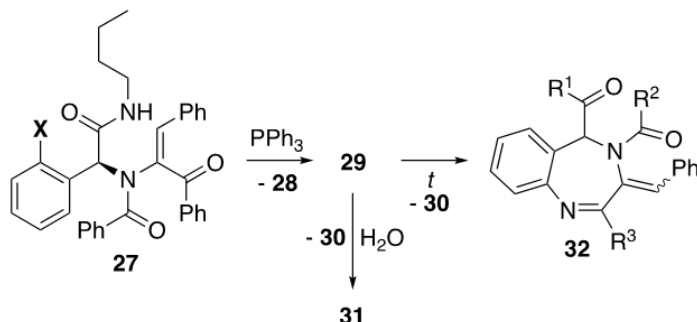
(e) **Choose** the reaction condition(s) and reaction partner that could synthesise an imine from compounds **25** and **26**.

A. Aniline (1 eq.), methanol (0.1 M), room temperature.

B. Aniline (1 eq.), TsOH (0.1 eq), toluene (0.1 M), Dean-Stark apparatus, reflux.

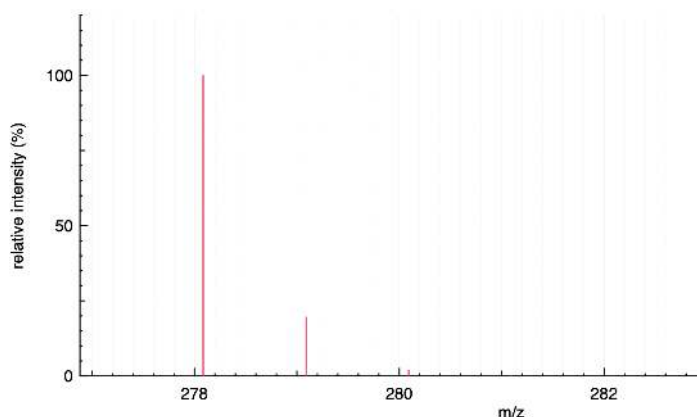
Condition(s) for 25 :	Condition(s) for 26 :
------------------------------	------------------------------

Another method for imine synthesis is described in the following scheme for the example of cyclic imine **32**. It is accompanied by formation of gas **28** and intermediate **29**. This reaction must be performed under anhydrous conditions because **29** can be hydrolysed by water; compound **30** and amine **31** are formed in this case. If intermediate **29** is heated, it is converted to desired compound **32**.

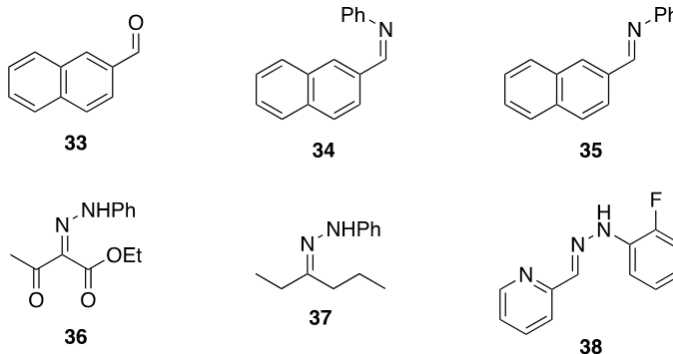


(f) **Draw** structures **27-32** including absolute stereochemistry. *Hints:* **X** is a functional group. Compound **27** can react with phenylacetylene (this reaction is catalysed by copper(I) iodide), and the reaction generates a five-membered ring that contains three nitrogen atoms. The mass spectrum of **30** is shown below.

MS of **30**



Imines and similar compounds sometimes have peculiar stereochemical properties.



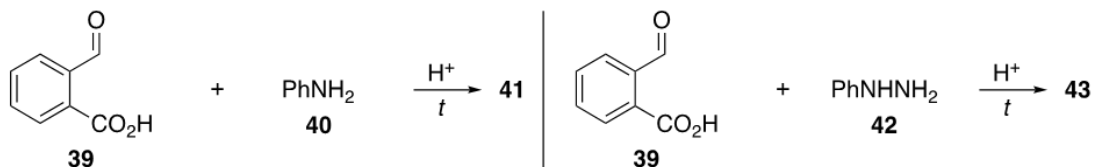


(g) **Choose** the correct statement(s) for each of the compounds above.

- A. This compound does not exist as there is an error in the structure.
- B. This compound has short lifetime as it is configurationally unstable.
- C. This compound is configurationally stable.
- D. This compound does not have stereoisomers.
- E. It can be transformed to another isomer by heating.
- F. It can be transformed to another isomer by irradiation with light.

33:
34:
35:
36:
37:
38:

Sometimes formation of C=N is accompanied with subsequent reactions.



t = heating

(h) **Draw** the structures of the products for the reactions if the configuration of the C=N bond is different in products **41** and **43**.



Episode V: The iminium salts strike back!

Imines have a C=N double bond, while in amines, bonds between C and N are all single bonds. In a later task, we will deal with pyridoxamine and imines obtained from pyridoxal. They both have a nitrogen atom. Let's consider the two model compounds: **1** and **2**.

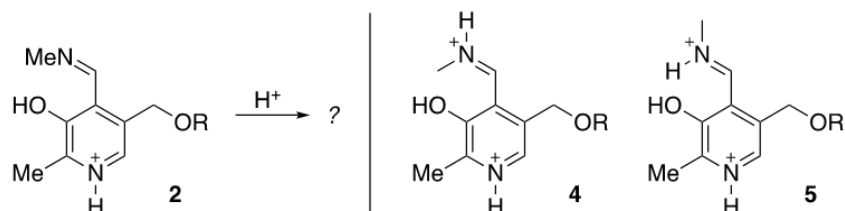


(i) **Choose** whether compound **1** or **2** is the stronger base.

Compound **2** can exist as several tautomeric forms: one is shown, while another has charge separation.

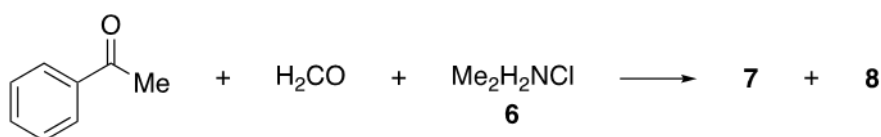
(j) **Draw** a second tautomeric form of **2**. **Draw** a resonance structure of this tautomeric form (the resonance structure should not have charge separation).

An iminium salt is formed when an imine is protonated. One example is presented below.



(k) **Choose** the more probable product structure (**4** or **5**) formed by protonation of compound **2** in an aprotic solvent.

Another way to make an iminium salt is reaction of a carbonyl compound with a secondary amine. In the example below, compound **6** is premixed with a more electrophilic carbonyl compound, and then a second compound with a carbonyl group is added after iminium formation. As a result, products **7** and **8** are formed.

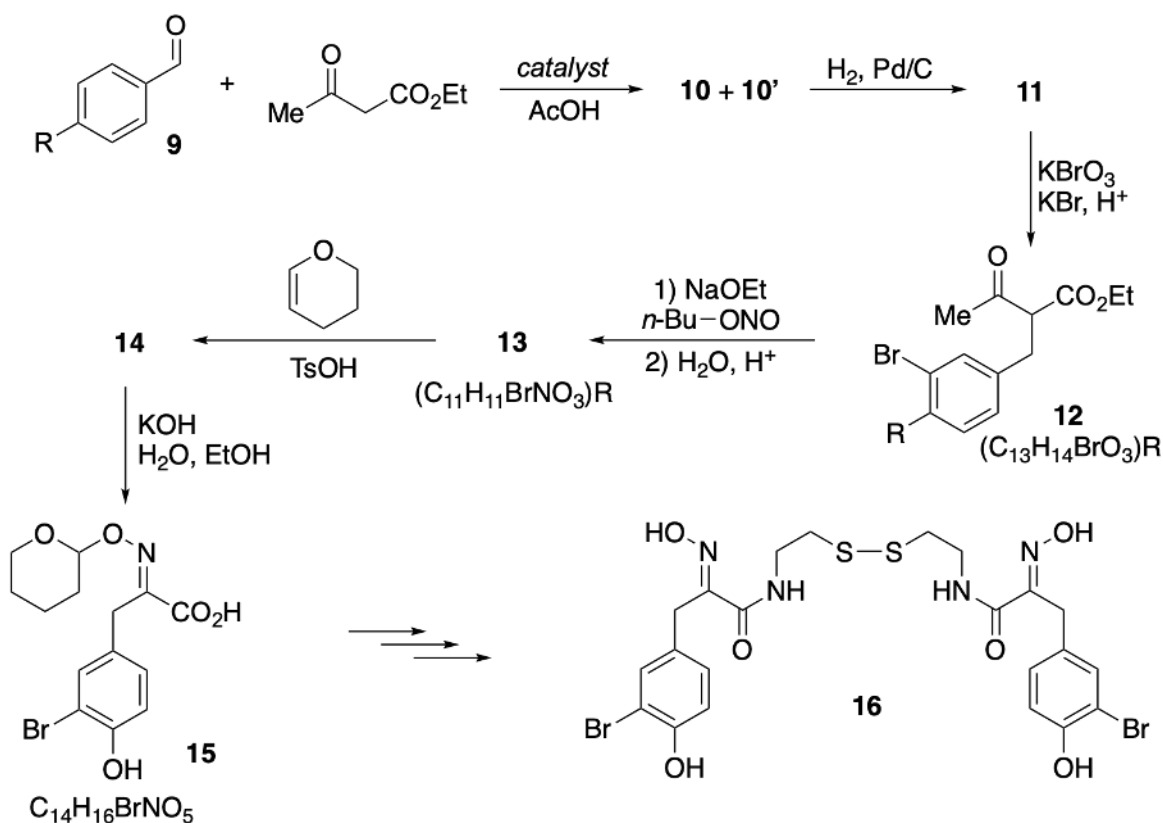




(l) **Draw** the structure of the intermediate iminium salt formed.

(m) **Draw** the structures of products **7** and **8**.

Iminium salts are often used in chemical transformations as active intermediates. The scheme below is presented for part of the total synthesis of compound **16**. This synthetic route includes an example of an iminium cation as an active intermediate.

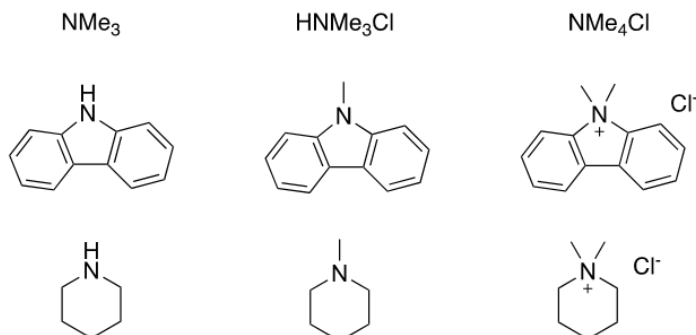


(n) **Write** the unknown substituent R in compound **9**.

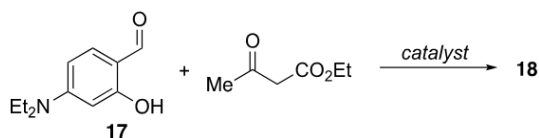
(o) **Draw** the structures of compounds **10**, **10'**, **11**, and **14**. You may use the abbreviation R as shown in the scheme.

(p) Compound **13** can exist as a mixture of two stereoisomers. **Draw** the structures of both possible geometrical isomers for **13**, if ethylacetate is liberated in the reaction from **12** to **13**.

(q) Compound **9** cannot be efficiently transformed to a mixture of isomers **10** and **10'** without a catalyst. **Choose** the best catalyst for this transformation from the list below.



Unlike compound **9**, compound **17** gives only product **18** when it reacts with ethyl acetoacetate under the same catalytic conditions.

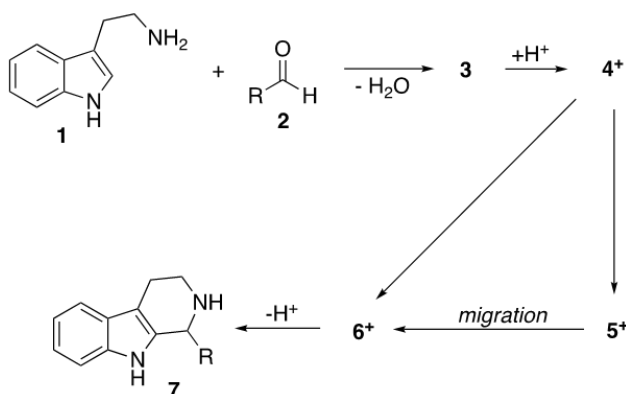


(r) Draw the structure of product **18**.



12. Imine`s guide to the biochemical galaxy

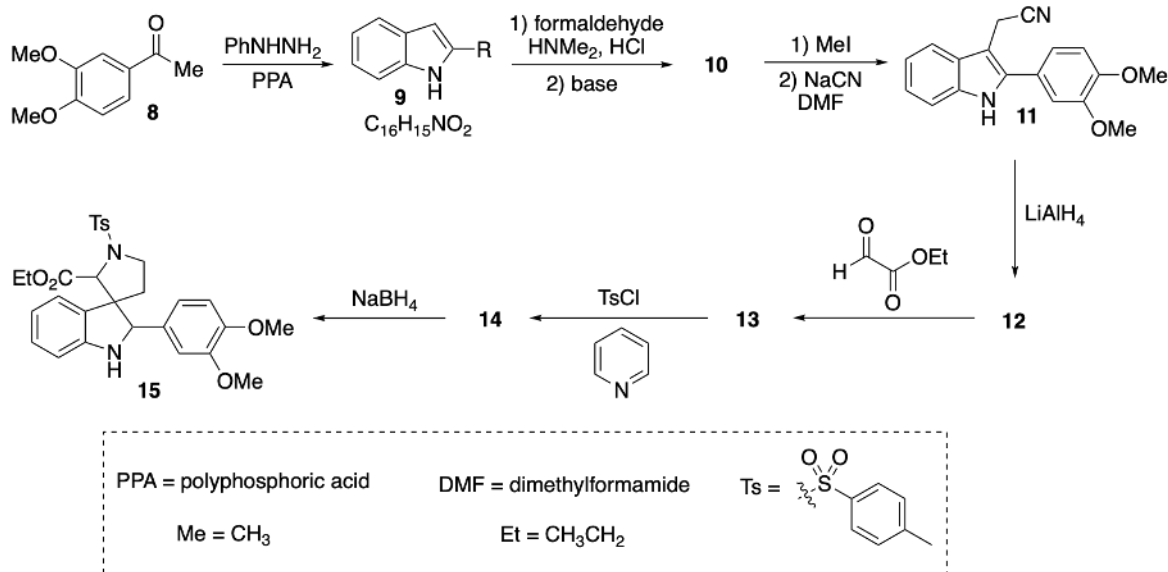
Imines are abundant chemicals both in the laboratory and in nature. Numerous organic reactions have been developed that utilise imines. One example is reaction X, for which the simplified mechanism is shown below (reaction X is the same reaction throughout this task). It is initiated by formation of **3**, which is followed by protonation. Cation **4⁺** can cyclise to **5⁺**, which yields **6⁺** after 1,2-migration. Alternatively, cation **4⁺** can directly undergo a 1,6-cyclisation to produce intermediate **6⁺**. The process is terminated by deprotonation, which yields product **7**.



(a) **Draw** the structures of compound **3** and intermediates **4⁺**-**6⁺**.

(b) **Draw** the most stable resonance form of **5⁺** and of **6⁺**, which demonstrate cation stabilisation.

Reaction X is robust which enables its use in total syntheses. Intermediates similar to **5⁺** can be trapped depending on their structure and other things present in the reaction. A part of a total synthesis is presented below as an example, where such an intermediate was stable. In this case, the tosyl group (Ts) was used as an electrophile instead of H⁺ to initiate reaction X.



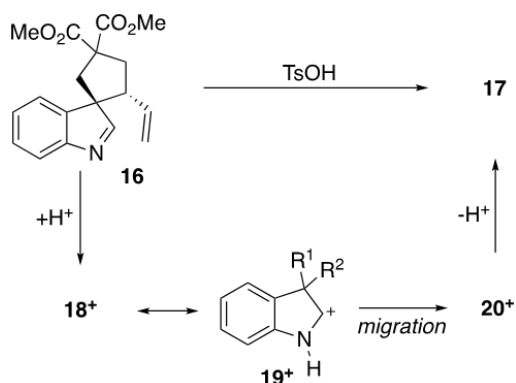
(c) **Draw** the structures of **9**, **10**, and **12-14**. Stereochemistry is not important in this part of the task. *Hint*: substituent R is a disubstituted aromatic ring.

(d) **Choose** the reason(s) why compound **14** is a final product. **Circle** the correct answer(s).

- A. Aromatisation is favourable.
- B. Aromatisation is unfavourable.
- C. Aromatisation is possible.
- D. Aromatisation is impossible.
- E. Deprotonation is possible.
- F. Deprotonation is impossible.
- G. Steric hindrance enhances the rate of six-membered ring formation.
- H. Steric hindrance decreases the rate of six-membered ring formation.

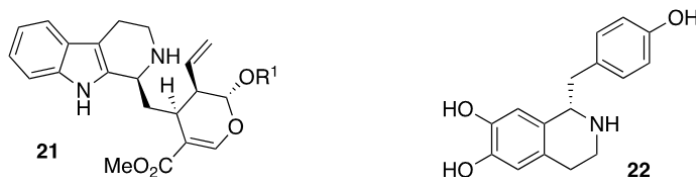
(e) How many stereoisomers does compound **15** have?

The hypothesis that six-membered products were obtained by migration was confirmed by many experiments. For example, compound **17** can be synthesised from **16** (the stereochemistry of the migrated fragment was retained). The mechanism of this transformation is presented below.



(f) **Draw** the structures of **17**, **18⁺**-**20⁺**. **18⁺** and **19⁺** are resonance structures. **Specify** the absolute stereochemistry where necessary.

As previously mentioned, reaction X occurs naturally in some organisms. Compounds **21** and **22** can be synthesised from amino acids through a series of enzymatic transformations. A single enzyme catalyses two sequential final steps: imine formation and reaction X.



(g) **Suggest** a biochemical pathway for the syntheses of both **21** and **22** using a pair of starting materials from those listed below: **choose** one amino acid and one aldehyde. The pathway should not exceed four steps; consider imine formation and reaction X as two separate steps.

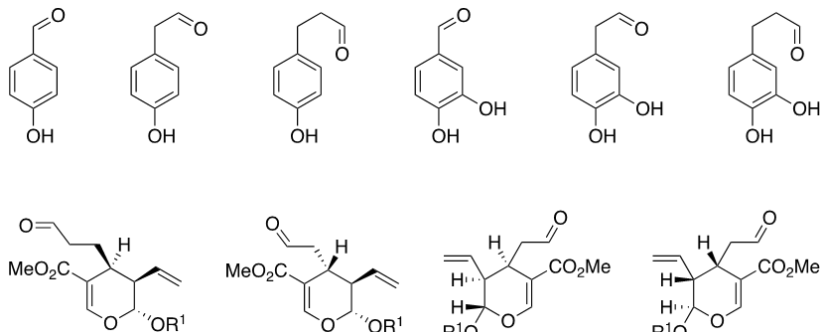


Specify the enzyme for each step using the following abbreviations:

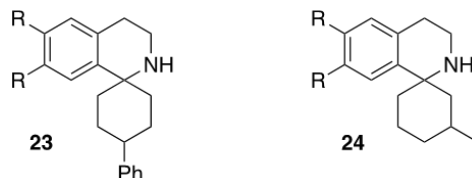
- DC – decarboxylase
- HD – hydroxylase
- IS – isomerase
- LS – lyase
- RD – reductase
- TR – transferase

Amino acids:

- Glycine
- Alanine
- Glutamic acid
- Serine
- Tyrosine
- Histidine
- Tryptophan



Compounds **23** and **24** can be synthesised by reaction X which is enzymatically catalysed. In this case, only one isomer is obtained out of many stereoisomers.

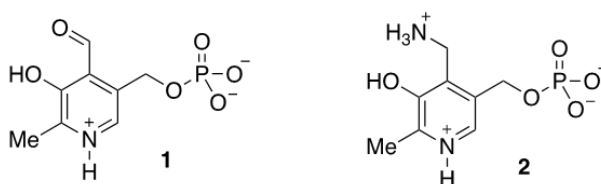


(h) How many stereoisomers do compounds **23** and **24** have?

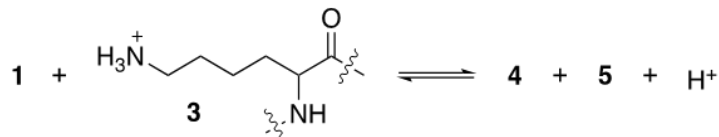


13. Schiff bases, the Universe, and biochemistry

Schiff bases are imines with an alkyl or aryl substituent on the nitrogen atom. They play an important role in many biochemical and biotechnological processes. Pyridoxal phosphate (PLP, **1**), an enzymatic cofactor derived from vitamin B₆, is one of the biologically important compounds that readily forms Schiff bases. A reaction cascade with an amine leads to PLP being transformed into pyridoxamine phosphate (PAP, **2**).

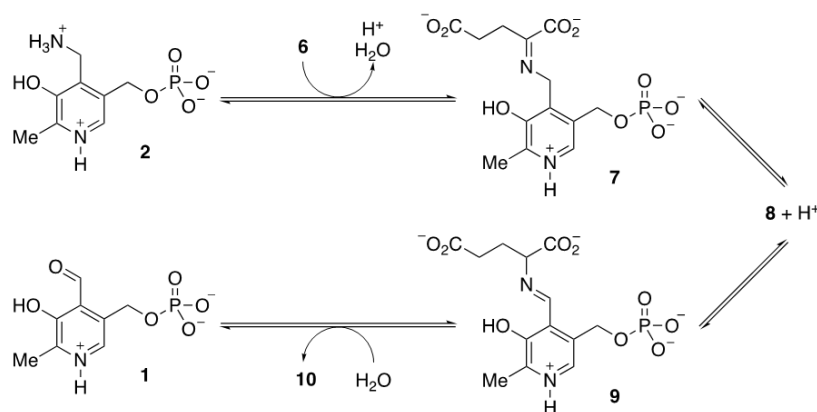


In many enzymes, the reactive aldehyde group of PLP does not exist in the free form. Instead, it forms a Schiff base product (**4**) with a specific lysine residue of an enzyme.



(a) **Draw** the structures of **4** and **5** using the lysine residue abbreviation **3**.

Transaminases (also referred to as aminotransferases) catalyse reactions between an α -amino acid and an α -ketocarboxylic acid. In the case of the enzyme E₁, the process starts with transamination of the PLP-lysine adduct **4** in the active site by alanine. The end of the catalytic cycle is given below.





(b) **Draw** the structures of **6**, **10**, and quinoid intermediate **8**.

(c) **Propose** the missing part of the E₁ catalytic cycle, clearly showing the reactants, intermediates, and the cofactor structure.

Beside transamination, amino acid racemisation and decarboxylation can be induced by PLP depending on the nature of the enzyme. All these processes start with Schiff base formation. Then the quinoid intermediate is obtained due to elimination of one of substituents at the α -carbon atom.

(d) **What** is/are the reason(s) that may cause elimination of a substituent? **Circle** the correct answer(s).

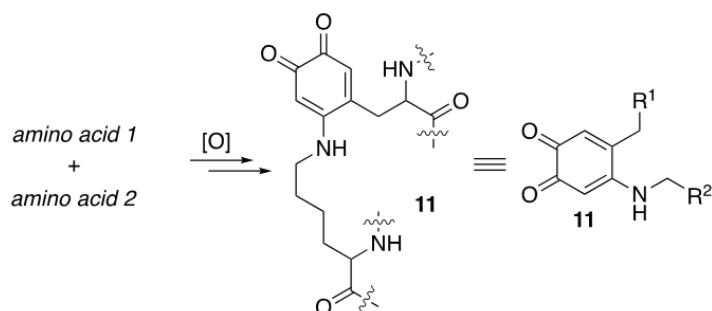
- Steric hindrance due to the tetrahedral environment of the α -carbon atom.
- Steric hindrance due to the planar geometry of the quinoid intermediate.
- Being electron deficient, the pyridinium ring withdraws electron density from the α -carbon atom.
- Being a strong nucleophile, the pyridinium ring attacks the carbonyl atom of the amino acid.
- Being a strong electrophile, the pyridine nitrogen atom attacks the carbonyl carbon of PLP.
- Being a strong nucleophile, the pyridine nitrogen atom attacks the carbonyl carbon of PLP.

(e) **Draw** the structures of the starting Schiff bases, quinoid intermediates, and the product(s) for:

- racemisation of L-alanine,
- decarboxylation of L-alanine.

Show the absolute stereochemistry where necessary.

Schiff bases are involved in inter- and intramolecular cross-linking of extracellular matrix proteins such as collagen and elastin. The carbonyl group necessary for the reaction with the amine group appears in an allysine residue due to oxidative deamination of the lysine residue during a post-translational modification. The latter process is catalysed by the enzyme E₂. Its cofactor (quinone **11**) is formed inside the active site of the enzyme from residues of two amino acids as shown below.

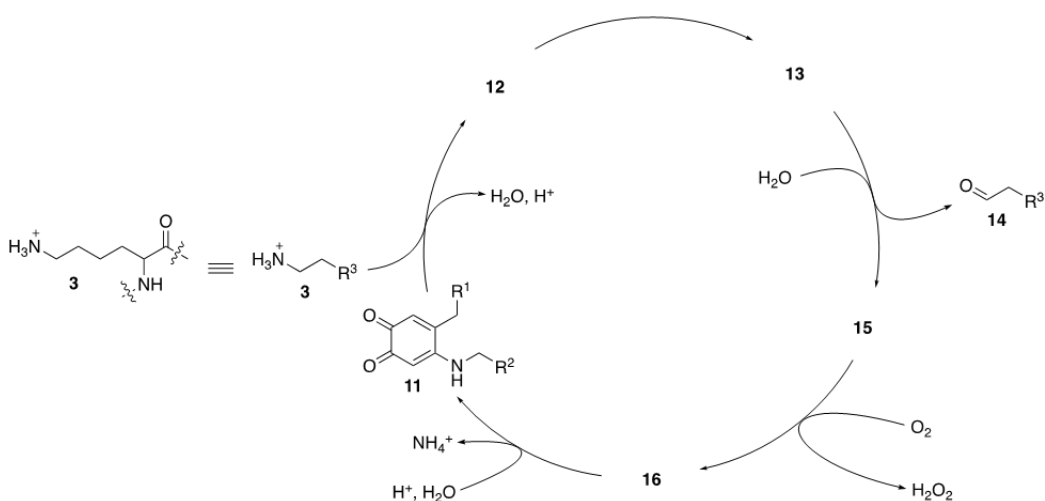


(f) **Select** which amino acid residues were used in the biosynthesis of **11**.

- a. Alanine
- b. Arginine
- c. Asparagine
- d. Glycine
- e. Methionine
- f. Tyrosine
- g. Tryptophan
- h. Lysine

(g) **Circle** the most electrophilic carbonyl group in **11**. **Draw** the resonance structure that confirms your hypothesis. **Use** the simplified structure of **11** shown above.

The catalytic cycle of E_2 for the transformation of lysine **3** to allysine **14** is shown below.



(h) **Draw** the structures of **12**, **13**, **14**, and **16**. Use the simplified formulae of **3** and **11** given above.

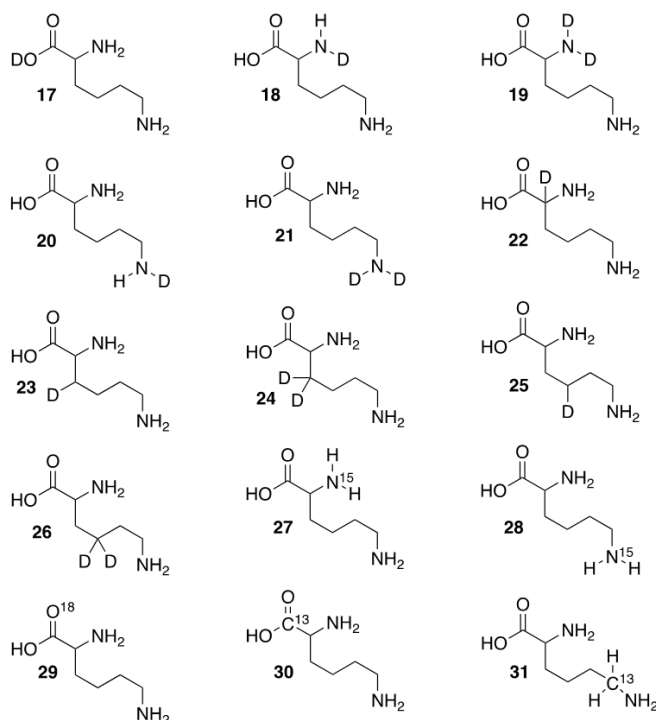


Isotope labelling is a method that allows us to track the origin of certain fragments after a chemical reaction. It is used extensively in biochemistry to study mechanisms of reactions.

Different versions of labelled lysine were prepared, and mass spectra (MS) were recorded for them using electrospray ionization in positive mode. The results of the analysis are presented below in the table.

Spectrum number	Ion $[M+H]^+$	Compound
1	145	
2	146	
3	147	
4	148	
5	149	
6	150	

(i) The mass spectra do not change for any of the labelled lysines after the samples are dissolved in methanol. **Choose** which of the labelled lysine compounds **17-31** could correspond to the given molecular ions in the table above.

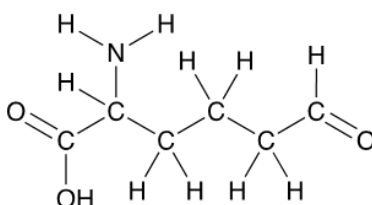


Desmosine **32** and isodesmosine **33** are two essential components of elastin. To biosynthesise them, one lysine and three allysine residues are needed to link four polypeptide fragments. One lysine residue and one allysine residue form Schiff base **34**, whereas the other two allysine residues undergo an aldol condensation that produces **35**. The two intermediates **34** and **35** finally react to give either **32** or **33**.

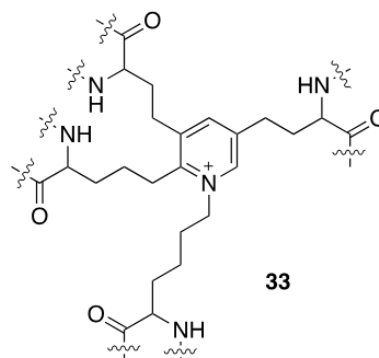
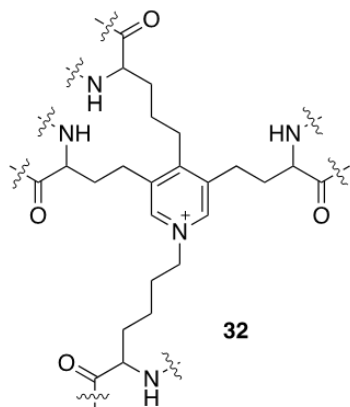
(j) **Draw** the structures of intermediates **34** and **35**.

To reveal the mechanism of the biosynthesis of **32** and of **33**, lysine labelled on the ϵ -carbon atoms was prepared. Then a sample of elastin was biosynthesised from it and then subjected to post-translational modification.

(k) **Circle** the labelled carbon atom in allysine which originated from ϵ -labelled lysine.



(l) **Circle** the labelled carbon atoms in **32** and **33**.



14. UAE's driving force

The United Arab Emirates has the sixth largest oil reserves in the world, mostly concentrated in the Emirate of Abu Dhabi. After extraction from oil reservoirs, crude oil is transported to oil refineries, where it is processed to produce various petroleum products. Around 40–50% of the crude oil is refined into gasoline. In this problem, you will explore the main steps in gasoline production. A typical gasoline is a mixture of alkanes, alkenes, cycloalkanes, and aromatic compounds with 4 to 12 carbon atoms. It is obtained by mixing different oil refining products introduced below into a gasoline blend.

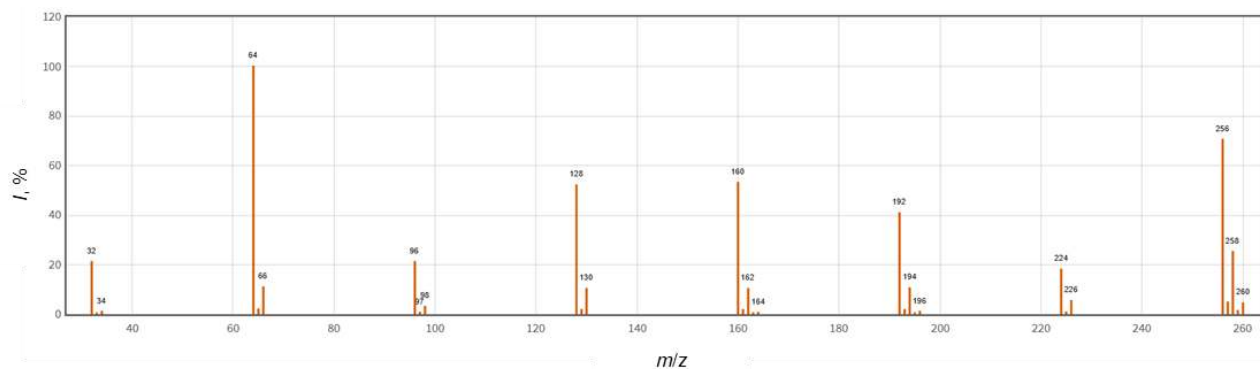
The refining process essentially starts with *atmospheric fractional distillation*, where crude oil is separated into fractions according to their boiling points. After this step, the residual oil is further separated using *vacuum fractional distillation* into heavier fractions with higher boiling points.

(a) **Number** the following compounds present in crude oil in order of increasing boiling point (1 – the lowest boiling point, 7 – the highest boiling point):

2,2-dimethylbutane	dodecane	pentane-1-thiol	propene	pentan-1-ol	hexane	benzene

The next step after distillation is *hydrotreatment*, which serves to reduce the content of element **X** in oil fractions. This step is required to prevent catalyst poisoning in further oil refining processes and to prevent acid rain forming as a result of the exhaust gases from fuel combustion. The *hydrotreatment* process is based on the catalytic reaction of **X**-containing compounds with hydrogen, producing gas **A**. $\frac{1}{3}$ of **A** obtained is then oxidised with air, producing gas **B**, which further reacts with the remaining $\frac{2}{3}$ of **A** to produce solid **C**.

The mass spectrum (electron impact ionisation was used as the ionisation method, *I* – relative intensity) of **C** and relative intensities of selected peaks ($[M]^+$ is the molecular peak) are shown:



Peak	$[M]^+$	$[M+1]^+$	$[M+2]^+$
$I, \%$	70.40	4.76	25.17

(b) **Identify** the element **X** and substances **A–C**, and **write down** the reaction between **A** and **B**.

There are four stable isotopes of element **X**. The isotope with a mass number A has the highest natural abundance of 94.85%. The heaviest stable isotope has a mass number of $A+4$.

(c) **Indicate** the mass numbers of the four stable isotopes of **X** and **calculate** the relative abundances of the three other isotopes.

After *hydrotreatment*, lighter oil fractions (“naphtha”) are subjected to *catalytic isomerisation* and *catalytic reforming* to produce “isomerate” and “reformate” components for gasoline blends with high octane ratings. A higher octane rating indicates that the fuel can withstand greater compression in an internal combustion engine reducing the probability of detonating prematurely. This resistance to detonation is essential for higher-compression engines to operate efficiently and produce greater power.

During *isomerisation*, linear alkanes are converted to branched isomers. During *reforming*, the most important reactions are the dehydrogenation of cyclohexane derivatives and the dehydrocyclisation of linear alkanes producing aromatic compounds.



(d) **Give** the total number of compounds in the “isomerase” produced from a mixture of butane, pentane, and hexane.

(e) **Draw** the structures of **all** the products of dehydrocyclisation reactions of hexane, heptane, and octane.

After *hydrotreatment*, heavier oil fractions are further subjected to *catalytic cracking* and *hydrocracking* to produce more valuable gasoline components. In these processes, long-chain hydrocarbons are broken into short ones. In *cracking*, typical products are alkanes and alkenes, while in *hydrocracking*, which is performed in the presence of hydrogen, the products are saturated hydrocarbons.

(f) **Determine** the molecular formula of the alkane, which gives a mixture of hexane and pentene during *cracking*, and octane as a single product during *hydrocracking*.

Propene and butene obtained during cracking are often used further to produce a gasoline component called “alkylate” by the alkylation reaction with isobutane under acid catalysis. The alkylate consists primarily of two hydrocarbons **D** and **E**, which have three and five non-equivalent carbon atoms in their structures, respectively. Hydrocarbon **E** is a reference standard for octane rating.

(g) **Draw** the structural formulae of **D** and **E**.

The gasoline components discussed above (naphtha, isomerase, reformat, cracked and hydrocracked gasoline, and alkylate) are mixed in different proportions to get gasoline with specific characteristics and quality. Other additives, such as oxygenates, stabilisers, detergents, antiknock agents, etc. are then added deliberately.

Antiknock agents increase the fuel's octane rating. Compound **F** was extensively used as an antiknock agent in the 20th century but is now mostly banned due to the toxicity of element **Y** in **F**. It is produced by the reaction between Na**Y** (sodium-**Y** alloy) and chloroalkane **G**, followed by the distillation of **F**. In its mass spectrum, one can observe the sequential loss of four fragments with m/z 29 from the molecular peak. The peak of the highest intensity (base peak) has m/z 237.

(h) **Determine** the element **Y**, substances **F** and **G**, and **write down** the reaction between Na**Y** and **G**.

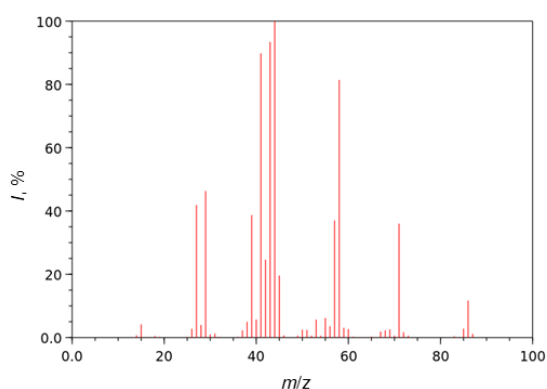


15. In search of an oasis in the desert

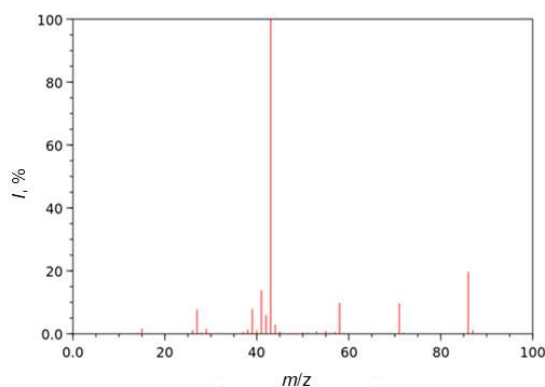
The United Arab Emirates University is located in the city of Al Ain, which is known for its rich history and lush greenery thanks to the largest oasis in the country. Just like searching for an oasis in a desert, in this problem, you will be challenged to find the structures of eight isomers from the large number of peaks their infrared (IR) and mass spectra shown.

Compounds **A–H** are all isomers of $C_5H_{10}O$. The mass spectra (electron impact ionisation, I_r % – relative intensity) of these compounds and the wavenumber of the strongest band in their IR spectra are given:

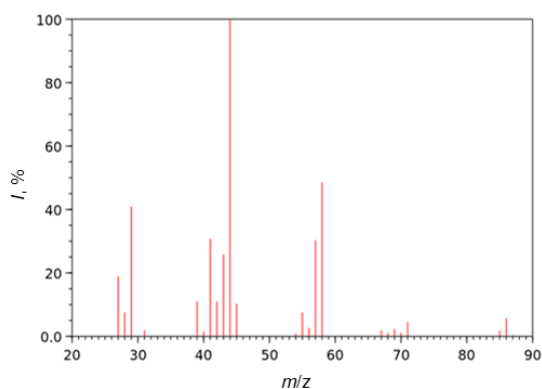
A (1728 cm^{-1})



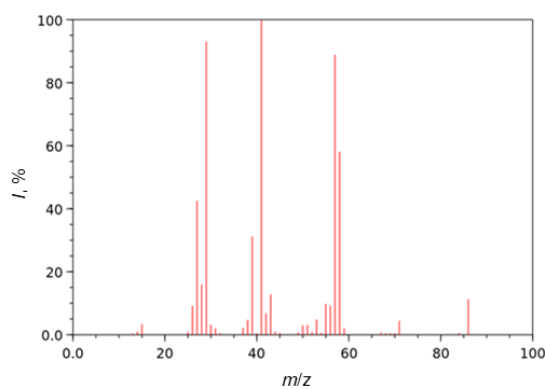
B (1717 cm^{-1})



C (1727 cm^{-1})

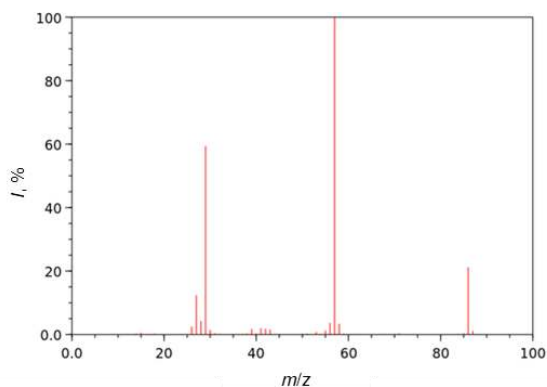


D (1728 cm^{-1})

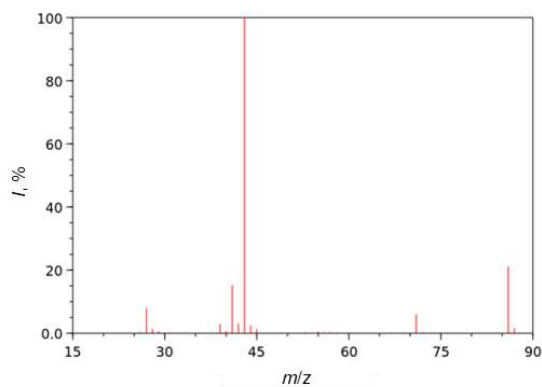




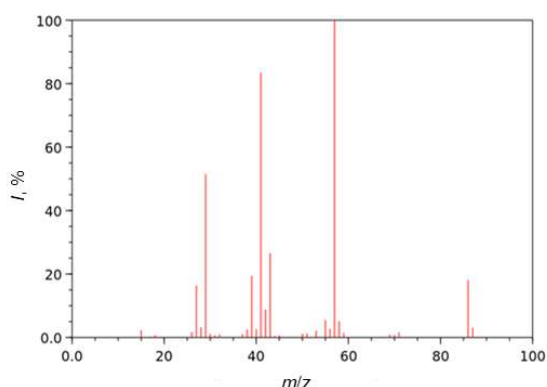
E (1720 cm^{-1})



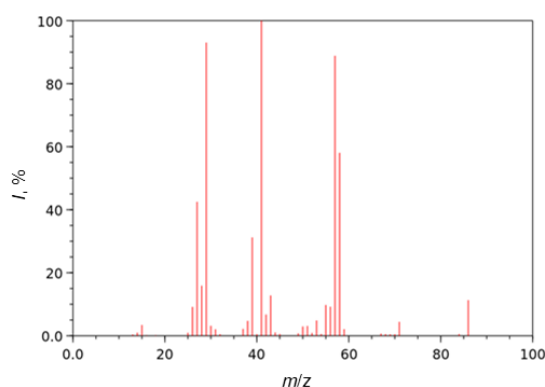
F (1718 cm^{-1})



G (1728 cm^{-1})

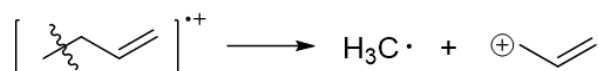


H (1728 cm^{-1})

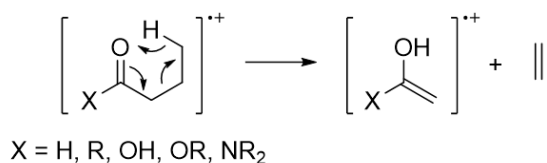


(a) **State** all the possible functional groups (or combinations of functional groups) that molecules with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$ can have.

Molecular ions formed during electron impact ionisation in a mass spectrometer are often in a high energy state and undergo dissociation into fragments. A typical fragmentation pathway is the cleavage of one of the bonds producing one charged and one neutral fragment. According to Stevenson's rule, the fragment with the lowest ionisation energy will possess a charge after the fragmentation, for example:



Another typical fragmentation pathway is some kind of rearrangement. For example, the McLafferty rearrangement is normally observed for carbonyl compounds but also alkenes, imines, etc:



(b) **Determine** the structures of isomers **A-H** using the data. If you are not able to assign a specific structure to the unknown isomer, list all your options.

The peak of the highest intensity in the mass spectrum is called a base peak. It is assigned 100% intensity, and the intensities of other peaks are calculated relative to the base peak.

(c) For each structure **A-H**, **suggest** a fragmentation pathway leading from the molecular ion to the species that gives the base peak in the mass spectrum.



16. Fullerenes and polyhedra

Fullerenes are allotropes of the element carbon that take the shape of polyhedra. C_{60} , the most famous member of the fullerenes, has the shape of a truncated icosahedron. This shape is far more commonly known as “a football”. Although approximately spherical when inflated, footballs are made from stitching together hexagonal and pentagonal pieces of fabric in the shape of the faces of the truncated icosahedron. In C_{60} , a carbon atom sits at every vertex of the truncated icosahedron, and there is a bond along every edge.



From left to right: (i) a truncated icosahedron; (ii) a football; (iii) C_{60} .

In 1758, the mathematician Leonhard Euler came up with a theorem describing the relationship between the number of vertices, v , the number of edges, e , and the number of faces, f , in a polyhedral shape:

$$v + f = e + 2$$

In a fullerene of formula C_n , as each carbon atom sits at the vertex of the polyhedron, we know that:

$$v = n$$

In fullerenes, assume that vertices are always trivalent (i.e., each carbon atom is bonded to three others) and all faces are either pentagons (p) or hexagons (h).

(a) In terms of n , **derive** an expression for the number of edges in a fullerene.

(b) In terms of n , **derive** an expression for the number of faces in a fullerene.

All fullerenes have 12 pentagonal faces ($p = 12$).



(c) **Show** mathematically that fullerenes have 12 pentagonal faces, and **derive** an expression for the number of hexagonal faces, h , in a fullerene, in terms of n .

Long before the discovery of fullerenes, in 1937 the mathematician Michael Goldberg considered a series of polyhedra constructed from pentagons and hexagons. These shapes are now known as Goldberg polyhedra. There are many possible structures for fullerenes, but the most symmetrical fullerene structures, including C_{60} , are Goldberg polyhedra.

A Class of Multi-Symmetric Polyhedra,

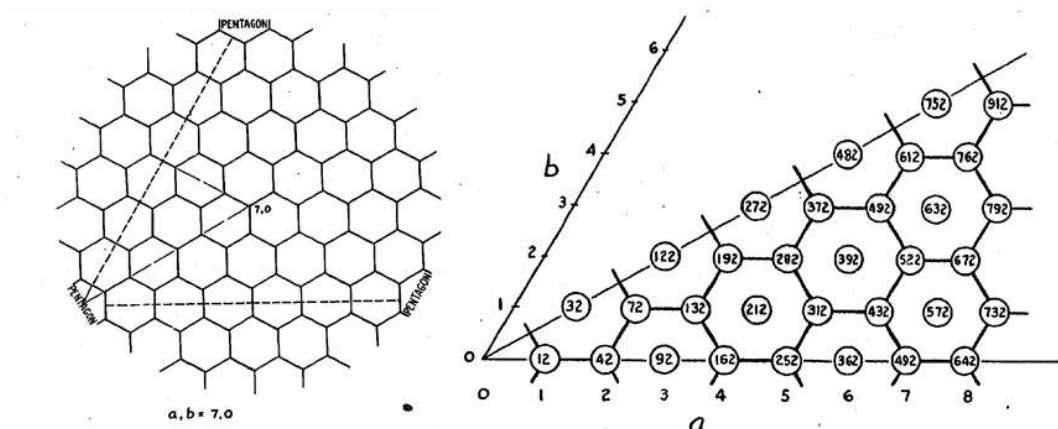
by

Michael GOLDBERG, Washington, D.C., U.S.A.

In a paper⁽¹⁾ by the author it was found desirable to consider a class of polyhedra, called medial polyhedra, which possess only trihedral vertices, and only pentagonal and hexagonal faces. It is shown in that paper that if the faces are more than eleven in number, then there are exactly twelve pentagons and the remaining faces are hexagons.

The introduction to Goldberg's 1937 paper.

The method to generate the series of structures can be seen in the following figures from Goldberg's paper. Goldberg imagined the surface net of the polyhedron being laid out onto a hexagonal lattice. The relative position of the nearest pentagons on the surface was then determined by two integers: a and b . On the left of the figure on the next page, to get from one pentagon to the nearest pentagon requires a move of seven faces in the a direction and a move of zero faces in the b direction. The polyhedron that would give this net would be denoted (7,0). On the right of the figure, it shows the total number of faces of the resulting polyhedra of various (a,b) values. All these polyhedra are potential fullerene structures.



Left: the relative position of pentagons on the surface net. Right: the total number of faces of Goldberg polyhedra of various (a,b) values.

(d) The smallest Goldberg polyhedron is $(0,1)$. It is a regular shape with only 12 faces, and we know these all must be pentagons. **What** is the common name for this shape?

(e) The $(1,1)$ Goldberg polyhedron is a truncated icosahedron, the shape of C_{60} fullerene. **Complete** the table below for C_{60} fullerene.

(a,b)	$v = n$	e	f	h
$(1,1)$				

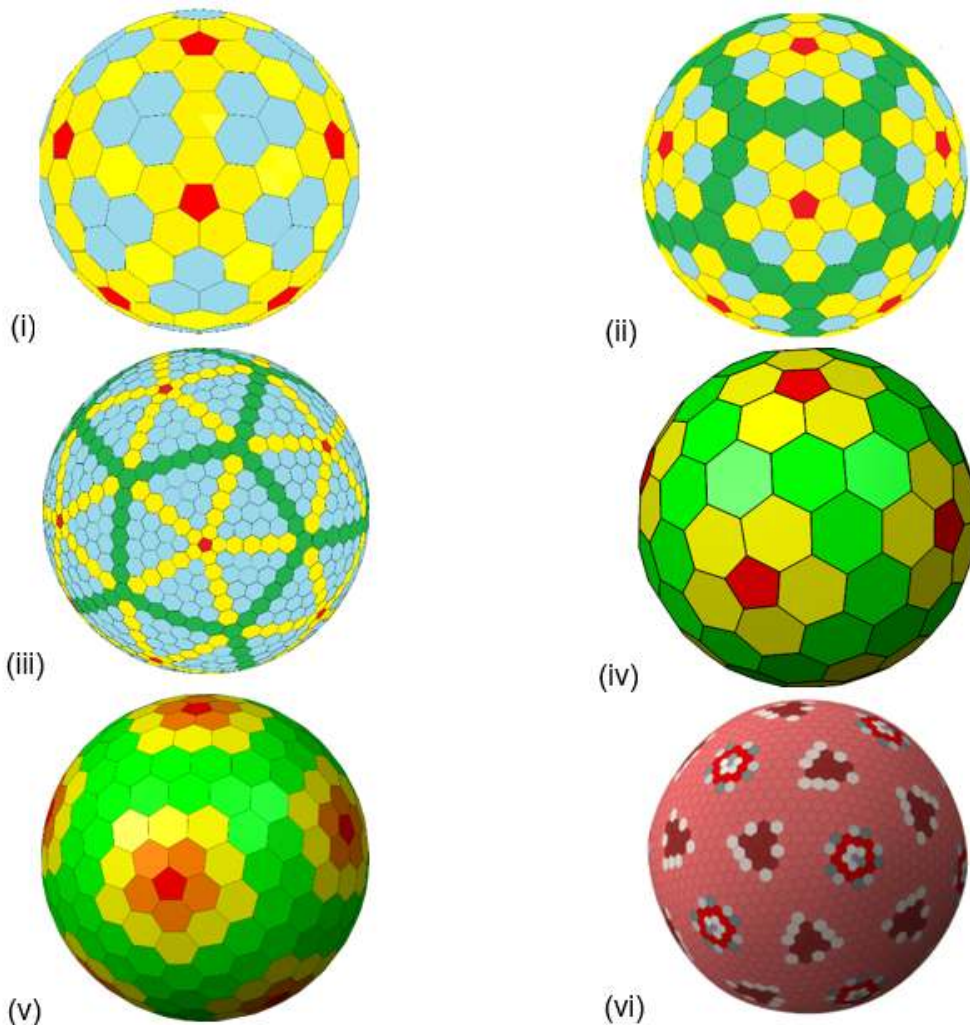
(f) **Complete** the table for other potential fullerene structures.

(a,b)	$v = n$	e	f	h
$(2,0)$				
$(2,1)$				
$(2,2)$				
$(3,0)$				
$(3,2)$				

The structure of six Goldberg polyhedra are shown below.



(g) **Determine** the values of (a,b) for each of the structures (i)-(vi).



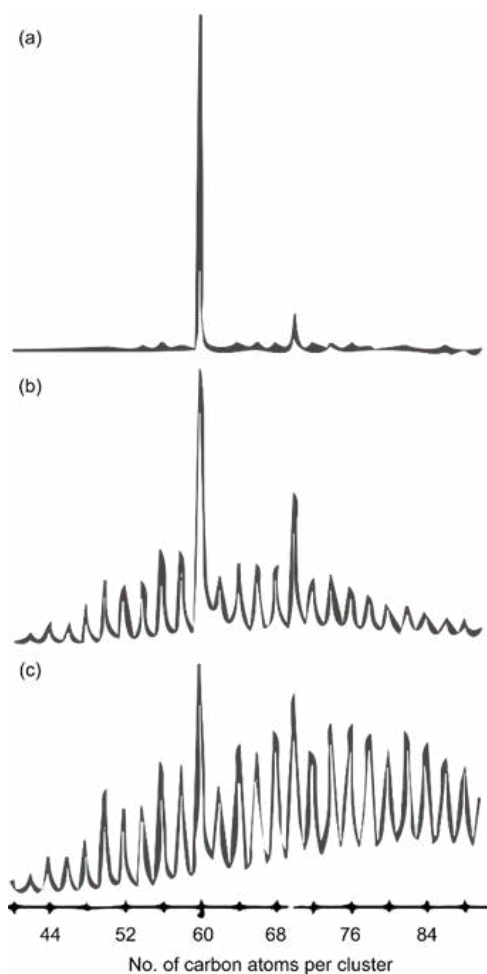
(h) **Which** of the following descriptors apply to the following pairs of Goldberg fullerenes? **Tick** all that apply.

- (i) (6,0) and (7,0)
- (ii) (7,0) and (5,3)
- (iii) (7,0) and (0,7)
- (iv) (5,3) and (3,5)



Allotropes	Stereoisomers	Diastereoisomers	Atropisomers
Isomers	Enantiomers	Conformational Isomers	Exactly the same

The discovery of fullerenes came many years after Euler and Goldberg. Although fullerenes had been predicted as stable for some time, the first detailed experimental evidence for fullerenes came in 1985 from mass spectra of the residue formed from the vaporisation of graphite in a helium atmosphere. Three authors on this paper, Harry Kroto, Robert Curl, and Richard Smalley would go on to win the Nobel Prize in Chemistry only 11 years later, indicating how quickly this discovery revolutionised chemistry and materials science.



The first detection by mass spectrometry of C_{60} , adapted from work of Kroto et al.



The mass spectra from the original paper are shown. It is possible to construct a fullerene shape for every even value of n from C_{20} upwards except for $n = 22$. However, some fullerenes are much more stable than others. The ratio of fullerenes formed in this work was dependent on the pressure of helium. In all cases C_{60} was the most abundant and C_{70} the second most abundant. C_{60} is the most stable fullerene as it is the smallest structure which does not require two pentagons to share an edge, and this relieves a lot of strain. C_{60} is also one of the highly symmetrical fullerene structures.

These mass spectra would be considered relatively “low resolution” by modern standards and are quite broad. One reason for this broadness is the presence of different isotopes of carbon. In mass spectra of small molecules, the predominant peak is always from the species containing all ^{12}C , as this is by far the most abundant isotope. However, as the number of carbon atoms increases, the intensity of the peaks containing one or more ^{13}C increases. These different isotopic species were not resolved in these first mass spectra of fullerenes and this is one reason behind the broadness of these peaks.

Assume an isotopic distribution of 98.94% ^{12}C and 1.06% ^{13}C .

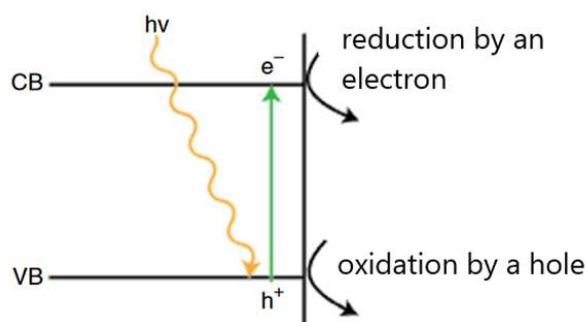
- (i) In the mass spec of C_{60} , **determine** the ratio of $^{12}\text{C}_{60}:^{12}\text{C}_{59}^{13}\text{C}$ peaks.
- (j) In the mass spec of C_{70} , **determine** the ratio of $^{12}\text{C}_{70}:^{12}\text{C}_{69}^{13}\text{C}$ peaks.
- (k) **Determine** the first fullerene for which the peak with one ^{13}C is more abundant than the peak with no ^{13}C .
- (l) **Determine** the first fullerene for which the peak with two ^{13}C is more abundant than the peak with one ^{13}C .



17. Photocatalysis

Photocatalysis is a way to utilise solar energy and carry out various useful but energetically unfavourable redox reactions, such as water splitting ($\Delta_r G^\circ_{298} = +237 \text{ kJ / mol of H}_2\text{O}$), carbon dioxide methanation ($\Delta_r G^\circ_{298} = +818 \text{ kJ / mol of CO}_2$), and others.

Common photocatalysts belong to one of the three classes of materials: transition-metal complexes, organic dyes, and semiconductors. Let's consider the latter class. When a semiconductor absorbs a photon with energy equal to or greater than the material's band gap, an electron is excited from the valence band (VB) to the conduction band (CB), generating an electron hole, h^+ , in the valence band. The excited electron can reduce a compound, while the positive hole can take up an electron from a compound and produce oxidised products. The overall process is a redox reaction at the surface of the semiconductor irradiated with light.



Not every semiconductor is suitable for a particular redox process. Both half-reactions – reduction by an electron and oxidation by a hole must be thermodynamically favourable, that is, the redox potential of a hole must be positive enough, while that of an electron – negative enough.

Consider two photochemical reactions: water splitting and carbon dioxide methanation by water. In both reactions consider an acidic medium.

(a) **Write** down the half-reactions occurring at the photocathode and photoanode, and the overall reactions.

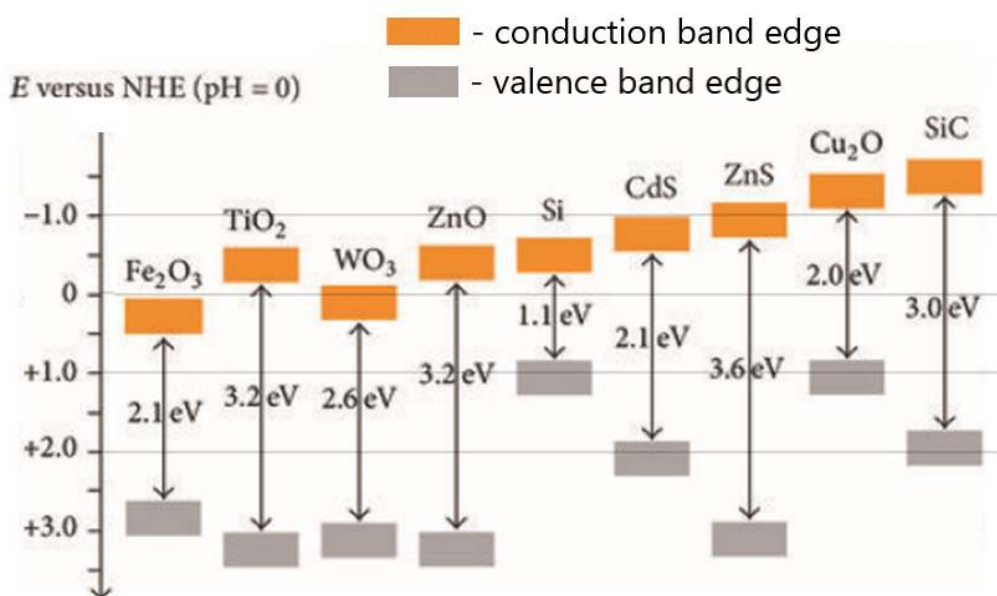


(b) If the acidic medium is replaced by a basic one, which of the following electrochemical properties for water splitting will change and which will not? **Mark** the correct cells.

Electrochemical property	will change	will not change
Overall reaction		
Cathode potential		
Emf		



The band energy diagrams of selected semiconductors and the table of standard reduction potentials for selected half-reactions are shown below.



Half-reaction	E° , V (pH 0)
$\text{O}_2 \rightarrow \text{H}_2\text{O}$	1.23
$\text{CO}_2 \rightarrow \text{CH}_4$	0.17
$\text{H}^+ \rightarrow \text{H}_2$	0

(c) Using these data, **determine** which of the listed semiconductors upon irradiation at pH = 0 are able to:

- oxidise water to O_2 ;
- reduce water to H_2 ;
- reduce carbon dioxide to methane
- both oxidise and reduce water.



The catalytic activity of photocatalysts is evaluated by the normalised reaction rates measured, e.g., in $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. However, to estimate the efficiency of light energy conversion other quantities are used. In homogeneous photochemistry, the quantum yield (QY) is defined as the number of product molecules to the number of absorbed photons ratio:

$$\text{QY} = \frac{\text{number of product molecules}}{\text{number of absorbed photons}} \cdot 100\%$$

However, in non-homogeneous photocatalytic systems, the actual number of photons absorbed is difficult to determine due to scattering and reflection of light. Therefore, the absorbed photon number is replaced by the incident photon number. In addition, the number of product molecules is replaced by the number of electrons transferred. The quantity calculated in this manner is referred to as the "apparent quantum yield" (AQY):

$$\text{AQY} = \frac{\text{number of electrons transferred}}{\text{number of incident photons}} \cdot 100\%$$

In a recent photocatalytic experiment, the catalyst (0.1 g) was dispersed in an aqueous solution of lactic acid and the solution was irradiated by a laser at 532 nm with a power of 200 mW. Hydrogen evolved from the solution at a normalised rate of $160 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

(d) **Calculate** the apparent quantum yield of water reduction.



18. Semiconductors

In the context of sustainable energy in the UAE, a country investing heavily in solar technology, semiconductors are promising materials for photovoltaic cells. Semiconductors are materials with electrical conductivity between that of a conductor (such as copper) and an insulator (such as rubber). This means they can conduct electricity under certain conditions, making them essential in modern electronics. One such material is cadmium telluride (CdTe), which is being explored for thin-film solar cells due to its efficiency in converting solar energy to electrical energy.

In this task, you will investigate the optical properties of CdTe, focussing on its band gap, molecular orbital structure, and how its properties affect solar cell efficiency in the UAE's sunlight conditions.

Molecular orbital structure

(a) CdTe is a II-VI compound semiconductor. Using MO theory, **discuss** how the overlap between Cd 5s and 5p orbitals with Te 5p orbitals leads to the formation of the conduction and valence bands.

Band gap calculation

The experimental band gap energy of CdTe is approximately 1.45 eV.

(b) **Calculate** the cutoff wavelength (λ_{cutoff}) for CdTe, beyond which the semiconductor becomes transparent to light. Use the formula:

$$\lambda_{\text{cutoff}} = \frac{hc}{E_g}$$

where E_g is the band gap energy (in Joules).

(c) **Relate** this cutoff wavelength to the solar spectrum in the UAE, where the maximum sunlight intensity is at approximately 550 nm. **How does** the band gap of CdTe make it suitable for photovoltaic applications in the UAE's sunlight conditions?



Optical absorption

CdTe has a strong absorption coefficient in the visible spectrum. Assume the optical absorption coefficient (α) at 500 nm is $2 \times 10^5 \text{ cm}^{-1}$.

(d) **Calculate** the penetration depth ($1/\alpha$), which is the distance at which the intensity of light decreases to $1/e$ of its original value.

(e) **Comment** on the significance of this property for the design of thin-film CdTe solar cells in the UAE.

Quantum dots: tiny particles for big applications

The Noble Prize in Chemistry 2023 was given to the scientists who discovered quantum dots (QDs). QDs are tiny semiconductor particles or nanocrystals, typically ranging from 2 to 10 nm in diameter. QDs are increasingly being researched as tunable materials for next-generation solar cells, particularly in places like the UAE, where solar energy is abundant. Quantum dots, which are semiconductor nanocrystals, exhibit unique optical and electronic properties due to quantum confinement. In this task, we will explore cadmium selenide (CdSe) quantum dots, analysing how their size influences the band gap, optical properties, and molecular orbital structure, and how these features are relevant for solar energy applications in the UAE.

Molecular orbital structure and quantum confinement

CdSe quantum dots are formed from cadmium (Cd) and selenium (Se), which typically form a bulk semiconductor material. In QDs, however, the small size leads to quantum confinement effects.

(f) **Explain** how the molecular orbitals of Cd and Se overlap to form the valence and conduction bands in bulk CdSe. **How does** quantum confinement alter this structure in smaller QDs?

(g) **How does** the particle size of QDs affect the band gap energy, and **why** is this tunability advantageous for solar cell applications, particularly in the UAE's environment?



Band gap calculation and size effect

CdSe QDs have a tunable band gap due to quantum confinement. The band gap increases as the size of the QD decreases. The band gap energy (E_g) for a quantum dot can be approximated using the following equation for the effective mass approximation:

$$E_g(R) = E_g^\infty + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon R}$$

Where, E_g^∞ is the CdSe bulk band gap (1.74 eV), R is the QD radius, m_e^* is the electron effective mass in CdSe ($0.13 m_0$), m_h^* is the hole effective mass in CdSe ($0.45 m_0$), $m_0 = 9.11 \times 10^{-31}$ kg, $e = 1.602 \times 10^{-19}$ C, ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m), ϵ is the dielectric constant of CdSe (10).

(h) For a quantum dot with a radius of 2.5 nm, **calculate** the band gap energy, $E_g(R)$.

(i) **How does** this band gap compare to the bulk band gap of CdSe? **What does** this indicate about the influence of size on the optical properties of CdSe quantum dots?

Optical properties and absorption

Quantum dots are known for their strong absorption in the visible spectrum, which makes them attractive for solar cell applications. The absorption wavelength, λ , is related to the band gap by:

$$\lambda_{cutoff} = \frac{hc}{E_g}$$

where E_g is the band gap energy (in Joules).

(j) Using the band gap calculated in part (h), **calculate** the cutoff absorption wavelength for the 2.5 nm CdSe QD.

(k) **Compare** this absorption wavelength with the peak solar spectrum intensity at 550 nm (green light) in the UAE. **What does** this tell you about the suitability of CdSe QDs for capturing solar energy in the UAE?



Exciton Bohr radius and quantum confinement

The exciton Bohr radius (a_B) represents the distance between the electron and hole in a bulk semiconductor. For CdSe, the exciton Bohr radius is approximately 5.6 nm. When the QD radius R becomes smaller than the exciton Bohr radius, quantum confinement effects become significant.

(l) **Compare** the radius of the QD from part (h) (2.5 nm) with the exciton Bohr radius of CdSe (5.6 nm).

(m) **Discuss** how the quantum confinement regime affects the electronic and optical properties of the quantum dots, particularly in relation to solar cell efficiency.

Solar cell application and design considerations

Quantum dots can be tuned to absorb different parts of the solar spectrum by varying their size. In quantum dot solar cells, one can layer QDs of different sizes to capture more of the solar spectrum. Given the intense sunlight in the UAE, consider the design of a multi-junction solar cell using different sized CdSe quantum dots.

(n) If you wanted to design a quantum dot solar cell that captures light from the visible spectrum (400-700 nm), **what range** of QD radii would you use? Assume the relationship between the QD radius and absorption wavelength follows this formula:

$$\lambda_{cutoff} = \frac{hc}{E_g(R)}$$

(o) **Discuss** the advantages of using quantum dots in solar cells for the UAE, focussing on their tunability and adaptability to the intense solar conditions.



19. Reverse combustion

Necessary information:

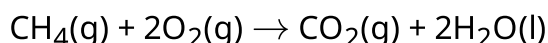
Assume that enthalpies and entropies of all reactions do not depend on temperature.

$$\Delta_{\text{vap}}S^\circ(\text{H}_2\text{O}) = 118 \text{ J / (mol}\cdot\text{K)}$$

$$\Delta_{\text{vap}}H^\circ(\text{H}_2\text{O}) = 44 \text{ kJ / mol}$$

Natural gas is used for heating, electricity generation, and as a chemical feedstock.

The reaction:



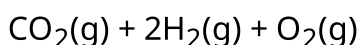
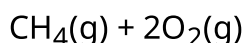
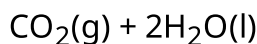
which accounts for ~20% of global CO_2 emissions, is highly favourable thermodynamically ($\Delta_r G^\circ_{298} = -818 \text{ kJ / mol}$) and releases much heat ($\Delta_r H^\circ_{298} = -890 \text{ kJ / mol}$). However, the reverse unfavourable process (carbon dioxide methanation) is also possible, but consumes much energy and is performed in several stages.

(a) **Draw** the graph of the dependence $\Delta_r G^\circ(T)$ for CO_2 methanation in the range from 298 K to 800 K.

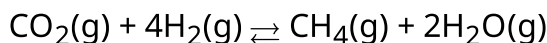
Synthetic methane production is already carried out through power-to-gas technology which employs photovoltaic cells to electrolyse water and generate hydrogen, which subsequently reduces CO_2 to CH_4 via heterogeneous catalysis. The CO_2 to CH_4 reduction ($\Delta_r G^\circ_{298} = -131 \text{ kJ / mol}$; $\Delta_r H^\circ_{298} = -253 \text{ kJ / mol}$) is performed using a Ni catalyst, supported on metal oxides, such as Al_2O_3 or ZrO_2 . Common operating temperatures are between 200 and 550°C, with pressures ranging from 1 to 100 bar.



(b) **Draw** the Gibbs energy diagram, showing the relative standard molar Gibbs energies of the following systems at 298 K and 1 bar:



(c) **Calculate** the equilibrium constant, K_p , for the reaction at 500 °C:



(d) The mixture $\text{CO}_2 : \text{H}_2 = 1 : 4$ was introduced into the reactor and heated to 500 °C. **At what total pressure** will the degree of conversion reach 90%?

Direct photocatalytic reduction of CO_2 to CH_4 by water is possible using either heterogeneous composite semiconductor catalysts or homogeneous dye catalysts. In one of the experiments, a CO_2 saturated solution in acetonitrile, containing an iron tetraphenylporphyrin dye together with a photosensitiser and trifluoroethanol, was irradiated with light at 420 nm and a constant power of 1.00 W. All light was absorbed. After the experiment, 1.1 mmol of CH_4 was obtained which corresponded to a quantum yield of 0.18%.

(e) **How long** did the irradiation take?



20. New drug formulation

In the UAE, researchers at a pharmaceutical company are developing a new drug formulation that needs to remain stable at sub-zero temperatures, especially when transported through cold desert nights or to mountainous areas such as Jebel Hafeet. A sample of 15 g of this drug is dissolved in 250 g of a solvent, which has the following properties:

- The molar mass of the solvent is 100 g/mol
- Freezing point of the pure solvent: $-15\text{ }^{\circ}\text{C}$
- Freezing point depression constant (K_f) for the solvent: $4.5\text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$
- Standard enthalpy of vaporisation of the solvent: $25.0\text{ kJ}\cdot\text{mol}^{-1}$
- Vapour pressure of the pure solvent at $-15\text{ }^{\circ}\text{C}$: 0.0075 atm
- The freezing point of the solution containing the drug: $-16.5\text{ }^{\circ}\text{C}$

(a) **Calculate** the molality of the drug in the solution. Assume that the Van't Hoff, $i = 1$.

(b) **Determine** the molecular weight of the drug.

(c) **Estimate** the vapour pressure of the solvent at a new freezing point after dissolving the drug, using the Clausius-Clapeyron equation and Raoult's law.

(d) **Discuss** how the freezing point depression and the vapour pressure changes affect the stability and transport of the drug in UAE's variable climate conditions.



21. Cloud seeding

"Cloud seeding is a chemistry experiment in the sky." - Robert Brown



Rainfall plays a crucial role in the environment, especially for arid regions such as the UAE which are characterised by their desert climate and scarce natural water resources. In this context, enhancing precipitation through scientific and technological interventions is of immense interest. Recently, the UAE has undertaken ambitious initiatives, such as cloud seeding, to induce and increase rainfall.

One of the forms of seeding technology is ice nucleating particles (INP), which induce ice formation in clouds, leading to rain through formation of small crystals of ice.

Let's consider that the average surface temperature in the UAE during July is 45 °C. The temperature of the atmosphere decreases linearly by 6.5 °C for each 1000 metres of altitude, and atmospheric pressure changes with height as:

$$\ln \frac{P_0}{P} = 0.139 \cdot h$$

where P_0 is the pressure at $h = 0$ and h is in km. The melting temperature of ice, T_m , changes with pressure as:

$$\frac{P}{T_m - 273} = -1.34 \cdot 10^4 \text{ kPa K}^{-1}$$

which comes from the Clausius equation and is the borderline between ice and liquid water on the phase diagram.

(a) **At what height** will ice clouds form, considering the average temperature in the UAE?

Even if the (p,T) condition for ice formation is met on the phase diagram, water can remain in the liquid state. This is known as supercooled liquid, and occurs since the nucleation (crystallisation) to form ice cannot begin due to a lack of impurities providing nucleation sites to initiate crystallisation.



(b) If we know that in the complete absence of any impurities, ice clouds are formed at a height of 12900 metres, **calculate** what temperature is necessary to force the crystallisation of water (i.e. supercooling temperature).

The role of INP compounds is to create nucleation centres to allow supercooled water to start to crystallise and thus precipitate as rain. The most common INP compound is silver iodide, as it has a structure similar to ice and can nucleate ice at temperatures up to -6°C .

Process	Energy (kJ/mol)
Sublimation enthalpy of silver ($\Delta_{\text{sub}}H^0(\text{Ag})$)	+285
Sublimation enthalpy of iodine ($\Delta_{\text{sub}}H^0(\text{I}_2)$)	+57
Bond dissociation enthalpy of iodine ($\Delta_{\text{diss}}H^0(\text{I}_2)$)	+150
Ionisation enthalpy of silver ($\Delta_{\text{ion}}H^0(\text{Ag})$)	+731
Electron affinity of iodine ($\Delta_{\text{aff}}H^0(\text{I})$)	-295
Formation enthalpy ($\Delta_fH^0(\text{AgI})$)	-62

The lattice energy of the INP compound affects the availability of nucleation sites at the molecular level. A stable lattice can provide energetically favourable sites for the alignment of water molecules, promoting the nucleation process. Also, compounds with high lattice energy have more defined and stable surfaces, which can facilitate the organised deposition of water molecules necessary for ice formation.

(c) Using a Born-Haber cycle, **calculate** the lattice energy formation of silver iodide ($\Delta_fH_{\text{lattice}}(\text{AgI})$) using the data given above.

We can evaluate the temperature of supercooling by employing concepts from classical nucleation theory and the Gibbs free energy change. The critical molar Gibbs free energy change for nucleation (ΔG_c) in the presence of a nucleating particle can be expressed as:



$$\Delta G_c = \frac{16\pi\gamma_{iw}^3}{3(\Delta G_v + \Delta G_{sl})^2}$$

where γ_{iw} is the interfacial tension between ice and water, ΔG_v is the volumetric Gibbs free energy difference, and ΔG_{sl} is the added energy from the lattice interaction.

For supercooled water, the volumetric Gibbs free energy difference is:

$$\Delta G_v = (\Delta H_f \cdot \Delta T) / T_m$$

where ΔT is the degree of supercooling (below 0°C) and ΔH_f is the enthalpy of melting of ice which is 335 kJ/kg. The additional interaction energy due to lattice energy can be approximated by:

$$\Delta G_{sl} = \alpha \cdot \Delta H_{lattice}$$

where $\alpha = 0.001$, and is a proportionality constant (for AgI) representing the interaction effectiveness of the lattice energy.

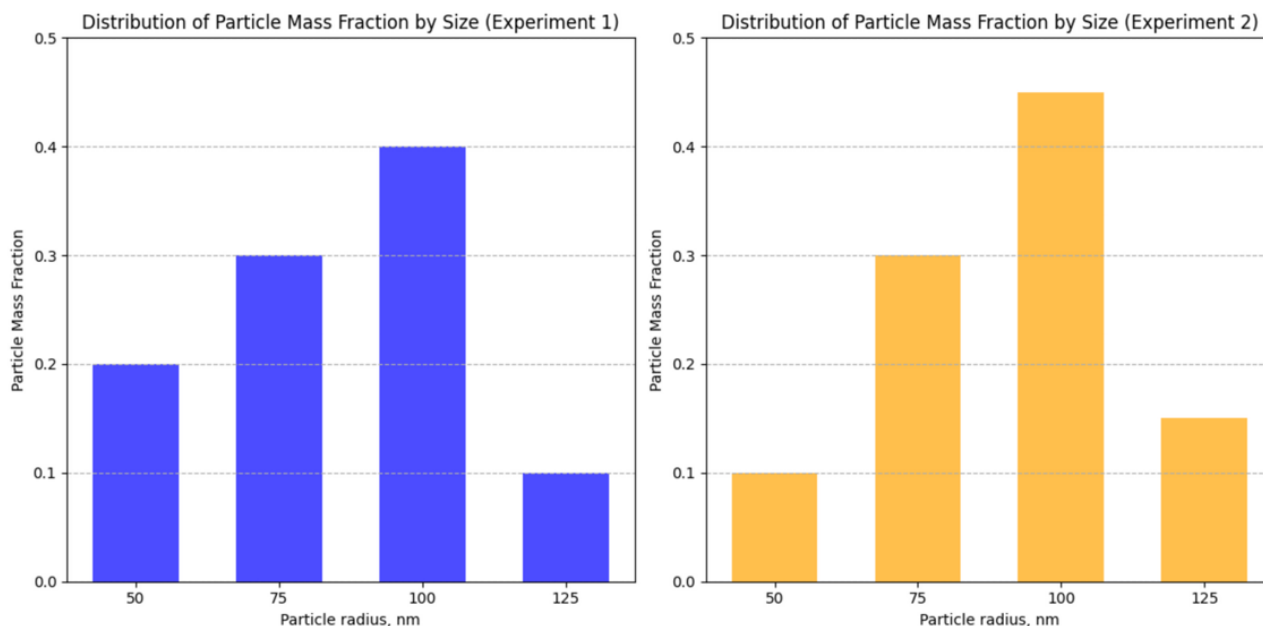
It is known that for the INP compound NaCl, the critical Gibbs free energy change for nucleation, $\Delta G_c = 108.3 \text{ kJ/mol}$ for a degree of supercooling of 10°C , whilst $\Delta G_{sl} = -350 \text{ J/mol}$.

(d) **Find** the critical Gibbs free energy change for nucleation of AgI at a degree of supercooling of 6°C .

(e) In **which regions** of the UAE is the possibility of having supercooled water in the atmosphere highest if there is no wind? **Circle** all that apply.

- A) above the city
- B) above the desert
- C) above the sea,
- D) in the air where aircraft regularly fly

The kinetics of cloud sediment depends on the particle size, which defines the total active surface of the compound. The sizes of two nanoparticles are rarely the same, and there is always a distribution of sizes. We will assume that all particles are spherical and that only a small part of the clouds turns into rain. To find the order of reaction, two experiments were carried out with a sample of 1.08 g of nanoparticles (blue distribution) and a sample with unknown mass (yellow distribution).



The initial rate of rain formation was 10% higher in the first experiment.

(f) **Estimate** the ratio of the surface atoms to the total number of atoms in a 100 nm particle, considering that average ion size is 0.3 nm, consider the surface covering is 0.80 and volume compacity is 0.70.

(g) Considering that in both experiments the number of 75 nm particles was the same, **calculate** the mass of the second (yellow) sample.

(h) **Check** if the order of the rain precipitation reaction for AgI is 0, 1 or neither.

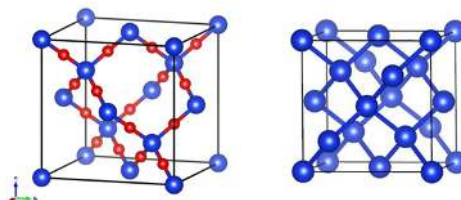


22. Kinetics of oxygen diffusion

"Data and semiconductors fuel the information age" - Jim Gray

Semiconductor transistors are essential in modern electronics for switching and amplifying signals. The formation of silicon dioxide (SiO_2) at the interface between silicon (Si) and oxygen (O_2) is a key step in semiconductor manufacturing to create the semiconductor-insulator interface.

Both SiO_2 and Si have cubic unit cells, as shown below.



The Si unit cell parameter is $5.43 \text{ \AA}$ and the Si-O bond length is $1.54 \text{ \AA}$. Assume that Si-O-Si bond angle is 180° .

- (a) **How many** SiO_2 units are located in a SiO_2 unit cell?
- (b) The volume of material increases upon oxidation. **Calculate** the ratio of the volume of SiO_2 to Si containing the same number of silicon atoms.

O_2	SiO_2	Si (silicon)
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In a 0.5 dm^3 chamber with initial pressure of O_2 of 1.5 bar at 923°C , an oxide layer was obtained on a 0.466 g Si wafer with surface 200 mm^2 under equilibrium conditions (silicon density is 2.33 g/cm^3). The Henry's law constant, $K = 2.35 \text{ M/bar}$. Assume that the surface area of the wafer remains constant, only its thickness is changing as it oxidises and the density of the SiO_2 layer formed is the same as for bulk SiO_2 . The Henry's law constant shows the partition of O_2 molecules between the gas phase and the solid phase at equilibrium. The only difference between a solid and a liquid is that in the solid, oxygen atoms are not homogeneously distributed. We will still express the quantity of oxygen in the solid as a molarity, as we generally do in liquid solutions.

- (c) **Calculate** the thickness of the wafer after equilibrium is reached.



(d) **Calculate** the thickness of oxide (l_{ox}) in this wafer assuming that there is a solid represent two pure phases SiO_2 and Si (as on the figure).

(e) **Recalculate** the thickness of oxide (l_{ox}) if the concentration of oxygen decreases linearly.

The kinetics describing the formation of an oxide layer of a particular thickness (l_{ox}) is known as the Deal-Grove equation for thermal oxidation.

$$l_{ox}^2 + A l_{ox} = B(t + \tau)$$

In this equation, **A** and **B** are empirical constants related to the oxygen diffusion and τ is the time corresponding to 'creating the initial oxide from bare silicon' and t is the growth time.

An experiment was performed to determine the values of **A** and **B** at 1200 °C. Substrates with different but known initial oxide thicknesses were exposed to thermal oxidation for exactly 1 h at 1200 °C. After the oxidation, the new oxide thickness was measured as shown in table:

Initial oxide thickness (nm)	Oxide thickness after 1 h (nm)
300	383
400	470
500	561
600	655
700	750

(f) **Calculate** the values of **A** and **B** for this experiment and give their units.

(g) **Use** a linear plot to **find** graphically the values of **A** and **B**.

(h) **Calculate** l_{ox} for $l_o = 2025$ nm.



The Deal-Grove equation has two limits: when the oxide thickness is high and when the oxide thickness is low.

(i) **Write** the limit equations for both cases and **indicate** which is which.

(j) **Verify** this limit for the following experimental data which were obtained at 1200 °C.

t , min	0	5	8	12
l_{ox}	1000	1012.6	1019.9	1030.0

In practice, the silicon substrate used in thermal oxidation is usually pre-doped to improve its electrical properties.

(k) For each of the dopants: B, P, As, and Ge, **indicate** which type of dopant they are:

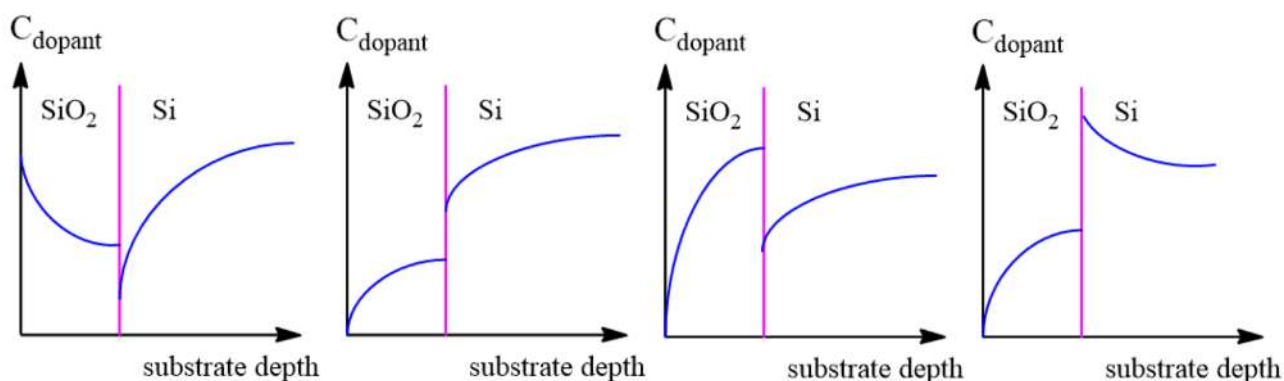
- A) n
- B) p
- C) n+p,
- D) neither n nor p

It is assumed that the dopant is uniformly spread throughout the substrate. The dopants have different solubility in Si and its oxide, which is given by the segregation coefficient, K :

$$K = \text{solubility of dopant in Si} / \text{solubility of dopant in SiO}_2$$

The concentration profile of the dopants across the substrate depends on the value of K as well as dopant diffusion in Si and SiO₂.

Boron atoms are more soluble in the oxide ($K_B < 1$) and they diffuse very fast inside it. On the other hand, phosphorus atoms are less soluble in the oxide ($K_P > 1$) and they diffuse very slowly inside it.



(l) For these two dopants, B and P, **choose** the correct concentration profile from the figure shown above.

A silicon wafer is covered by a thin layer of silicon dioxide. Initially, the total amount of dopant is 1×10^{15} atoms/dm². At equilibrium at 1200 K, the segregation coefficient, $K = 0.70$. The total thickness of the Si layer is 300 nm and the SiO₂ layer is 100 nm.

(m) **Calculate** the concentrations C_{SiO_2} and C_{Si} .



23. Molecular orbitals of diatomics

The three ionisation energies below each belong to one of the three diatomic molecules: N_2 , O_2 , and NO .

9.26 eV	12.07 eV	15.5 eV
---------	----------	---------

- (a) **Draw** an MO diagram for each of the three molecules. You only need to consider overlap of the 2s and the 2p orbitals.
- (b) **Using** these MO diagrams, **indicate** which ionisation energy belongs to which molecule.
- (c) **Order** the following compounds in order of their O-O bond length and **calculate** the O-O bond order for each case: O_2 , KO_2 , BaO_2 , and $[\text{O}_2][\text{Pt}^{\text{V}}\text{F}_6]$.

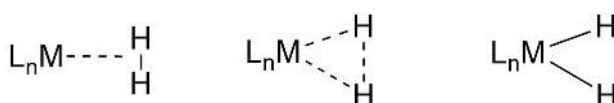
The O-O bond length in H_2O_2 is 1.48 Å whereas the O-O bond is only 1.22 Å long in O_2F_2 .

- (d) **Explain** this observation using MO theory. Hint: consider only the O-O moiety for each molecule and pay attention to its partial charge.



24. Coordination chemistry of dihydrogen

Molecular hydrogen (H_2) can act as a ligand in certain transition metal complexes. In these complexes, the hydrogen atoms can have a different character depending on the metal as well as the nature of other ligands coordinated to the metal atom. They can range from a dihydrogen complex where the H_2 molecule keeps its bond, to dihydrido complexes when the bond between the two H atoms is completely broken. There are intermediate states as well, of course.



(a) **Draw** an MO energy diagram for the interaction between the metal d orbitals and the molecular orbitals of H_2 . **Indicate** which orbitals on the metal are of correct symmetry to interact with each molecular orbital of H_2 . **Indicate** how the energy levels of the orbitals change, and **draw** cartoon representations of these orbitals. Assume the H_2 bond/axis lies along the x-axis and the M- H_2 bond/axis lies along the z-axis.

Consider the two complexes below. One of them can be classified as a dihydrogen complex, whereas the other can be classified as a dihydrido complex.



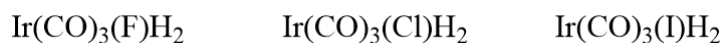
(b) **Determine** which complex belongs to which class. Provide a reason based on the MO diagrams you have drawn.

(c) **Arrange** the following complexes in order of decreasing H-H bond distance:



(d) **Draw** the interactions of the ligand p-orbitals with the metal d-orbitals in M-X where X is a halide.

(e) **Arrange** the following complexes in order of decreasing H-H bond distance:

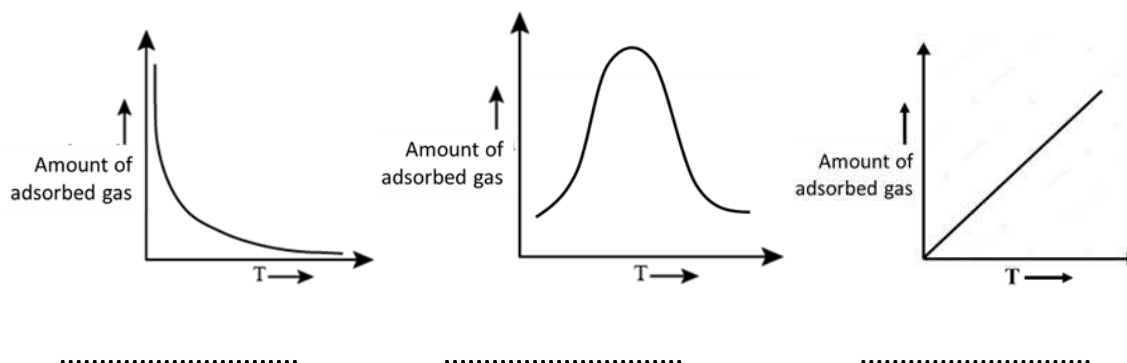




25. Adsorption and heterogeneous catalysis

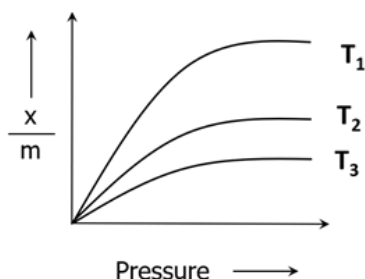
Catalysis has become a cornerstone of the chemical industry today where >80% of the commercially produced chemicals rely on catalytic processes. A large number of important catalytic processes depend on heterogeneous catalysts, where the catalysts are usually solids and the reactants are gases or liquids. They work by adsorbing and activating reactant molecules on their surfaces allowing them to react. Heterogeneous catalytic processes involve three main steps: (i) adsorption and activation of the reactant molecules; (ii) reaction between adsorbed molecules; and (iii) desorption of the products. Adsorption of reactants on the surface of a catalyst can be through weak interactions, mainly van der Waals forces (physical adsorption) or through strong interactions with formation of chemical bonds with active sites on the surface (chemical adsorption), which results in weakening or breaking bonds within the adsorbate molecules promoting reactions. Very often, the catalyst is fabricated in the form of nanoparticles deposited on the surface of high-surface-area porous powder as a support, such as active carbon and zeolites. The performance of a catalyst depends on various chemical and physical characteristics including the particle size of the active phase, commonly metal or metal oxide particles, and the surface area of the support.

(a) (a) The plots (A-C) below represent the extent of adsorption (the amount of gas adsorbed) vs. temperature. **Which graph** represents physical adsorption and **which graph** represents chemical adsorption? **Write** your answers in the space under the plots.





The amounts of physically adsorbed gas per unit mass of adsorbent (x/m) vs. pressure (P) are plotted below for a gas at different temperatures.



(b) **Order** the values of T_1 , T_2 , and T_3 according to increasing temperature.

Answer: < <

(c) **Which** of the following statements is correct for the spontaneous adsorption of a gas? Circle the correct statement.

- (i) ΔS is negative and therefore, ΔH must be highly positive;
- (ii) ΔS is negative and ΔH must be highly negative;
- (iii) ΔS is positive and ΔH must be negative;
- (iv) ΔS is positive and ΔH must be highly negative.

The extent of adsorption depends on various characteristics of the adsorbent and the adsorbate molecules. One of these characteristics is the acid-base properties of the adsorbate molecules and the adsorbent surface. On the surface of metal oxides, the metal ions act as acidic sites and the oxide ions act as basic sites. The acid-base behaviour of a metal oxide depends on various factors including the metal ion size and oxidation state.

(d) Assuming that the acid-base interaction is the decisive factor, **select** the two solids from the following list that would show the highest tendency to adsorb NH_3 molecules.

Carbon, MgO , Al_2O_3 , CaO , SiO_2 .

(e) The surface area of porous solids such as metal oxides is usually measured by physical adsorption of a monolayer of N_2 gas. In one experiment, a 0.5 g sample of a catalyst adsorbed 50 mL of N_2 (at 273.15 K, 1 atm) forming a monolayer of adsorbed N_2 molecules. The effective surface area occupied by one N_2 molecule is $0.16 \times 10^{-14} \text{ cm}^2$. **Calculate** the surface area (in m^2) per gram of the catalyst.

A wide range of chemical industries depend on active metal catalysts where nanoparticles of the active metal are used on a high surface area support.

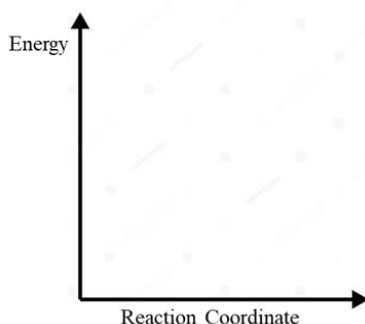
(f) **What** is the purpose of using nanoscale-sized metal particles? **Circle** all reasons that apply:

- (i) Nanoparticles provide higher surface areas.
- (ii) Nanoparticles generally provide more active sites on the surface.
- (iii) Nanoparticles allow the use of smaller amounts of expensive metal catalysts.
- (iv) Nanoparticles are easier to prepare than large particles.
- (v) Nanoparticles are more thermally stable than large particles.

Partial oxidation of CH_4 to produce CO and H_2 with a H_2/CO molar ratio of 2 (referred to as syngas) is a common conversion route for natural gas. It is an exothermic reaction that can be catalysed by nanoparticles of noble metals as well as non-noble metals such as Ni and Co.

(g) **Write** a balanced chemical equation for this reaction.

(h) On the figure below, **plot** a curve that represents the reaction coordinate diagram for the catalysed reaction, i.e., how the energy changes over the course of the reaction for the catalysed process. On the same graph, use a dotted line to **plot** the reaction coordinate diagram for the uncatalysed process.



During a catalytic alkene hydrogenation reaction over noble metal catalysts such as Pt particles, H_2 molecules are adsorbed on the catalyst's surface.



- (i) **Is** the interaction of H_2 with the catalyst chemisorption or physisorption?
Explain your answer.
- (j) **Describe** the type of metal-hydrogen interaction as “van der Waals interaction only”, “ σ -type bonding only”, or “ σ - and π -bonding”.
- (k) **Explain** your answer to part (j) by showing appropriate sketches of possible overlap between the metal and hydrogen orbitals.



26. Nitrogen chemistry

Nitrogen forms diverse structures, ranging from simple diatomic molecules, to polyatomic ions such as nitrate. It plays a vital role in biologically relevant macromolecules such as proteins and nucleic acids. Beyond Earth and under extreme conditions, nitrogen can even form exotic structures, such as polymeric nitrogen or extended nitrogen networks.

Liquid N_2O_4 ($d = 1.44 \text{ g/mL}$) was passed through a column packed with 30 g of solid KCl, with a flow rate of about $117 \mu\text{L/min}$. During the first 3 h, the only product coming out the other side of the column was yellow gas **A** (reaction 1). After that time, brown gas **B** started exiting the column, signalling the completion of the reaction. At this point, the solid remaining in the column was a mixture of KCl and solid **C**. Yellow gas **A** can react with FeCl_3 to make salt **D** (reaction 2), containing 24.5% iron by mass.

- (a) **Identify** compounds **A-D**.
- (b) **Write** equations for reactions 1 and 2.
- (c) **Draw** the Lewis structure of compound **C**.
- (d) **Draw** an MO diagram for the cation of **D**.
- (e) **Calculate** the mass of the remaining solid in the column.

Compound **A** reacts with isoamyl alcohol ($\text{C}_5\text{H}_{11}\text{OH}$) producing organic compound **E**. The reaction of **E** with hydroxylamine in the presence of NaOEt/EtOH results in the formation of the carbon-free sodium salt **F** (reaction 3), which upon addition of AgNO_3 gives a white, shock-sensitive precipitate **G**. Dissolving 1.00 g of **G** in excess concentrated HCl makes 1.04 g of a new white precipitate **H** as well as compound **I**. Compound **I** can be extracted with ether.

- (f) **Identify** compounds **E-I**.
- (g) **Write** the equation for reaction 3.
- (h) **Draw** a Lewis structure for the most stable form of the anion in **F**.



When an aqueous solution of hydrazine is added to an aqueous solution of cobalt(II) perchlorate, pink salt **X** precipitates which is unstable and decomposes upon shock or heating. The only solid decomposition product is elemental cobalt. When 500 mg of **X** is fully decomposed, 83.3 mg of Co is produced along with a gaseous mixture, which has a volume of 517 mL at 400 K and 1.0 bar.

(i) **Identify** compound **X**.

(j) Knowing that the cation in **X** is made of extended linear chains, **propose** its structure.

(k) **Write** an equation for the decomposition of compound **X**.

Nickel also makes an analogous compound (**Y**), which is less stable than its cobalt counterpart.

(l) **Calculate** the mass percentage of Ni in **Y**.

In order to measure the activation energy for the decomposition reaction of the Ni vs Co compounds, the two samples were heated at different constant temperatures and their mass loss was carefully recorded as a function of time.

Mass Loss	After 1 min	After 2 min
Co (400 K)	1.770 mg	3.540 mg
Co (420 K)	2.125 mg	4.250 mg
Ni (400 K)	2.655 mg	5.310 mg
Ni (420 K)	3.010 mg	6.020 mg

(m) **Calculate** the mass difference resulting from decomposition of 1 mol of the: i) Co, and ii) Ni compounds.

(n) **Calculate** the E_a of decomposition for both compounds.



(o) According to the data below, **select** the rate determining step in the decomposition of these compounds:

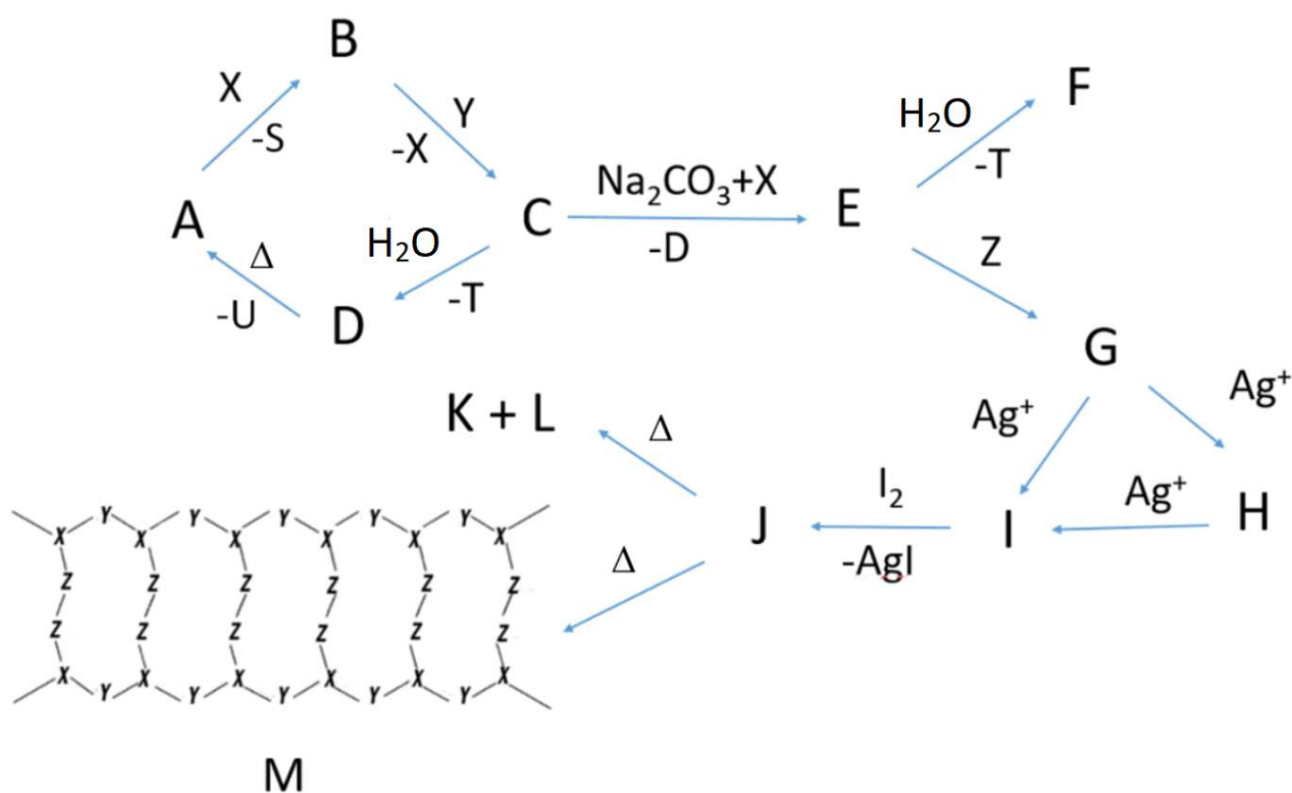
	Co	Ni
M-N bond lengths in $M(\text{NH}_3)_6^{2+}$	2.1 – 2.2 Å	2.0 – 2.1 Å
Electronegativity of M	1.88	1.91

- A) M-N bond breaking
- B) N-N bond breaking
- C) N-H bond breaking
- D) N-Cl bond breaking
- E) M-Cl bond breaking
- F) M-O bond breaking

27. Hot desert of unknown unknowns

"Somewhere, something incredible is waiting to be known." - Carl Sagan

The structure of polymer **M** contains atoms of three different types of elements: **X**, **Y**, and **Z**. Its synthesis is shown below. Please note that the structure shown for **M** only shows the connectivity between atoms **X**, **Y**, and **Z** and does not show the bond order.



Note elements **X**, **Y**, and **Z** also appear at other places in the scheme.

Hints:

- i. Compounds **J**, **K**, and **L** contain just the same three elements as polymer **M**.
- ii. Substances **A** and **B** and gases **S**, **T**, and **U** are binary. Gases **S** and **T** are lighter than air, and gas **U** is composed of the same elements as gas **S**.
- iii. Substance **D** is a white crystalline substance insoluble in water.
- iv. Compounds **A-D** contain the same metal, and its mass fraction in **A** is 71.4%.
- v. Salt **F** contains 47.05% oxygen and substance **H** is a complex salt containing an anion with a linear geometry.



- vi. Substance **J** is unstable and easily decomposes into equimolar amounts of substances **K** and **L** (with no other by-products). Alternatively, **J** polymerises to form substance **M**. From 2.025 g of substance **J**, 0.634 g of substance **K** is obtained.
- vii. During the polymerisation of **J** in ethanol, a gradual colour change occurred from yellow to deep red.

- (a) **Identify** all the unknown compounds.
- (b) **Write** equations for all chemical reactions that occur.
- (c) **Draw** the Lewis structures of the anions present in **B**, **C**, and **D**.
- (d) **Compare** the relative ease of formation of Ag^+ complexes with the anions of substances **E** and **G**.
- (e) **What** is the name of the anion present in compound **C**?



28. Analytical chemistry of the chalcogens

Sulfur chemistry is fascinating due to sulfur's ability to form diverse compounds with oxygen, such as sulfates and sulfites, and various polysulfide chains. These connections allow for versatile structural and chemical properties, making sulfur integral to many biological, industrial, and environmental processes.

Sulfite containing compounds are widely used as a broad spectrum preservatives (E220–228) to prevent microbial spoiling and browning reactions across a wide range of consumable products.

(a) **Calculate** the oxidation state(s) of S in the following ions: SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_2\text{O}_7^{2-}$, $\text{S}_2\text{O}_8^{2-}$, and SCN^- .

(b) **Draw** the Lewis structures of these ions.

Sulfite ions in aqueous solution can be obtained by dissolving sulfur dioxide. Let's assume that the initial solution is pure water with no sulfur containing ions and it comes into contact with air at standard pressure which contains 0.015 ppm (in volume) of SO_2 . Assume that there is a big excess of air and equilibrium is reached. The equilibrium between $\text{SO}_{2(g)}$ and $\text{SO}_{2(aq)}$ is defined via Henry's law constant.

(c) **Calculate** from what pH value the concentration of sulfite ions in this solution reaches a value of 10^{-6} M. **What** is the solubility of SO_2 at this pH?

$$K(\text{Henry})=1.3 \text{ mol}/(\text{L}\cdot\text{atm}); \text{p}K_{a1}(\text{H}_2\text{SO}_3) = 1.80 \text{ and } \text{p}K_{a2}(\text{H}_2\text{SO}_3) = 7.20$$

(d) **At what** pH value will the S be 99.990% in the form of sulfite ions?

Very often in solutions redox reactions with sulfite ions occur which changes the solution pH value. Let's modulate such a system by mixing a sulfite solution with a hydrosulfate solution.

(e) **Calculate** the pH of a solution which was obtained by adding 50 mL of Na_2SO_3 (0.100 M) to 150 mL of NaHSO_4 (0.080 M). Neglect the SO_2 gas-liquid equilibrium.

$$\text{p}K_{a2}(\text{H}_2\text{SO}_4) = 2.00$$



Polyphenol oxidase (PPO) is the enzyme which produces highly reactive *o*-quinone intermediates from phenol derivatives. The *o*-quinone promotes a cascade of reactions leading to the formation of undesirable coloured products. Sulfite has a dual action in that it acts directly to inhibit the enzyme but also reduces the *o*-quinone to the more stable 1,2-dihydroxybenzene.

Standard potentials: $E^0(o\text{-quinone}/1,2\text{-dihydroxybenzene}) = 0.69 \text{ V}$ and $E^0(\text{SO}_4^{2-}/\text{SO}_3^{2-}) = 0.24 \text{ V}$. Potentials are given within the same reference.

(f) **Indicate how** the potential of each couple change upon increasing the pH (increase/decrease/no change). Consider only the change in concentration of H^+ .

(g) **Analyse** if 0.099 M, 0.100 M, or 0.101 M of sulfite ions being in the same solution with 0.100 M of *o*-quinone could reduce it completely. Consider here that complete reduction is reached when the concentration of *o*-quinone becomes less than 10^{-9} M.

(h) **How** does the pH of the solution influence this redox reaction?

The nucleophilic capabilities of the sulfite anion also play a role in maintaining food quality through the inhibition of non-enzyme, Maillard-type browning. The condensation of amine functional groups (from free amino acids or protein) with the aldehyde group of reducing sugars leads to the corresponding N-substituted glycosylamines, which are then transformed to ketosamines in two steps. Sulfite anions modify the groups which could react with amines, thus avoiding the condensation.

(i) **Draw** the reactions of this process. **Abbreviate** the amine as RNH_2 and reducing sugar aldehyde as $\text{RCH}(\text{OH})\text{CHO}$.

Both of these reactions are very sensitive to pH which should neither be too low nor too high. Additionally, one of the reactions is very sensitive to which acid is used because of its redox properties. The use of HNO_3 can cause problems.

(j) **Write** chemical reactions with H^+ (and HNO_3) responsible for such behaviour.

The Association of Analytical Chemists has established a standard reference method for sulfite measurement, based on the Monier and Williams method. In this method, the sample is refluxed in acid (Equation (1)). This is done under a flow of



nitrogen, with the carrier gas bubbled through a 3% peroxide solution (Equation (2)). The final solution is then titrated with standardised sodium hydroxide solution (Equation (3)). Another way to analyse sulfite ions is the potentiometric titration with iodine (Equation (4)).

(k) **Write** all mentioned reactions.

Sulfite ions can be obtained by reduction of sulfate ions. It is known that selenate ions are not reduced by chloride ions, but are reduced to selenite by bromides and to Se by iodides. It is known that selenate ions are stronger oxidants than sulfate ions.

(l) **Which** halide ions (Cl^- , Br^- , I^-) could or could not reduce sulfate ions to sulfite ions?

Selenic acid (H_2SeO_4) is a rather strong oxidising agent, stronger than sulfuric acid or bromine but weaker than chlorine. It is capable of oxidising gold to the +3 oxidation state. Elemental gold can be dissolved in water-free selenic acid at high temperatures and pressures. In the early 1900s, the product of this reaction was thought to be $\text{Au}_2(\text{SeO}_3)_3$, but around a hundred years later in the early 2000s, that was found to be incorrect. The other product of this reaction is selenous acid (H_2SeO_3).

(m) **Write** a balanced equation for the reaction if the product was actually $\text{Au}_2(\text{SeO}_3)_3$.

Depending on the reaction conditions, the product can be either compound **A** or compound **B**, both of which contain only gold, selenium, and oxygen. Two different 200 mg samples of finely powdered metallic gold were mixed with 350 mg of pure selenic acid and heated in an autoclave under different conditions, leading to the production of either 401.4 mg of **A** or 337.0 mg of **B** (assuming 100% yield). After filtering the precipitated **A** or **B**, the remaining solution was neutralized and poured into an aqueous solution containing excess KI. In both cases (**A** or **B**), 20.3 mL of 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$ solution was needed to titrate the released iodine. Note: in these conditions, selenate ions are inert.

(n) **Identify** compounds **A** and **B**, and write balanced chemical equations for their production.

29. Vibrational modes

The modes of a molecule describe the possible motion of the atoms in the molecule that do not result in a change in position of the centre of mass. If the bond length increases and decreases during a vibration then the mode is called stretching, whereas if the bond angle (between three atoms) changes, it is called bending.

(a) **How many** modes of vibration does the CO₂ molecule have?

(b) **How many** bands are expected in its infrared spectrum?

(c) **Does** the spectrum of SO₂ show the same number of bands?

The simplest theoretical model for a vibrating molecule describes two atoms bound to each other through a weightless spring (harmonic oscillator). According to this model, the frequency of the vibration can be calculated as:

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

Where k is the force constant of the chemical bond, and μ is the reduced mass: (m_1 and m_2 being the mass of atoms 1 and 2, respectively).

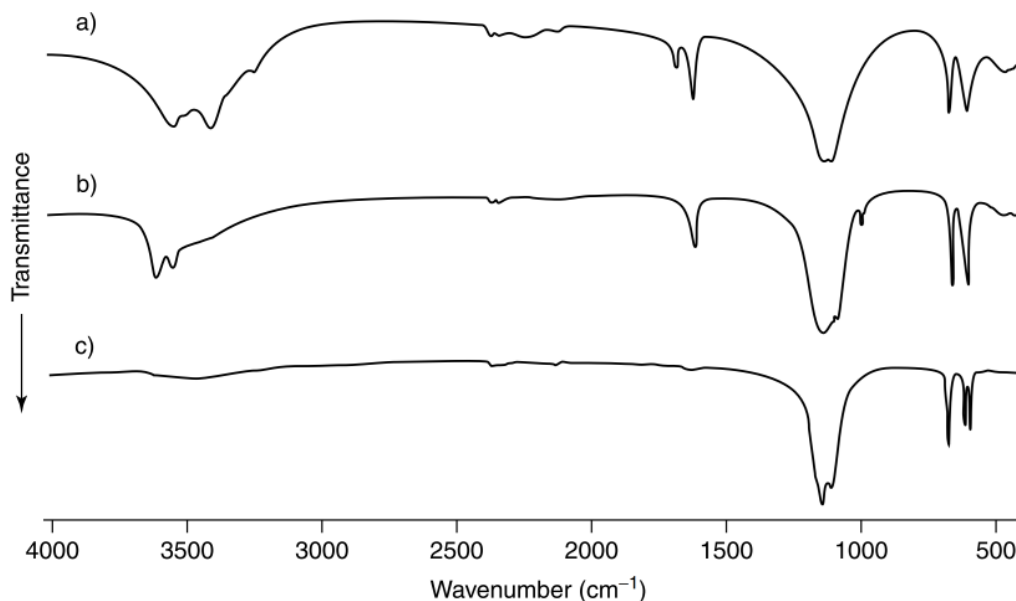
$$\mu^{-1} = m_1^{-1} + m_2^{-1}$$

(d) In the infrared spectrum of SO₂ the band assigned to the asymmetric stretching appears at 1151 cm⁻¹. **Calculate** the force constant, k , of the S=O bond.

(e) **Estimate** the energy of the asymmetric stretch.

(f) **Would** the wavenumber of the band be different if the S-O bond were single? **Explain** why.

Calcium sulfate can be found in three forms: anhydrite (anhydrous calcium sulfate), plaster of Paris (calcium sulfate hemihydrate) and gypsum (calcium sulfate dihydrate). The following picture shows the spectra of the three forms of calcium sulfate.



(g) **Is it possible** to distinguish which bands correspond to water and which bands correspond to the sulfate anion? **Determine** the spectrum that corresponds to anhydrite.

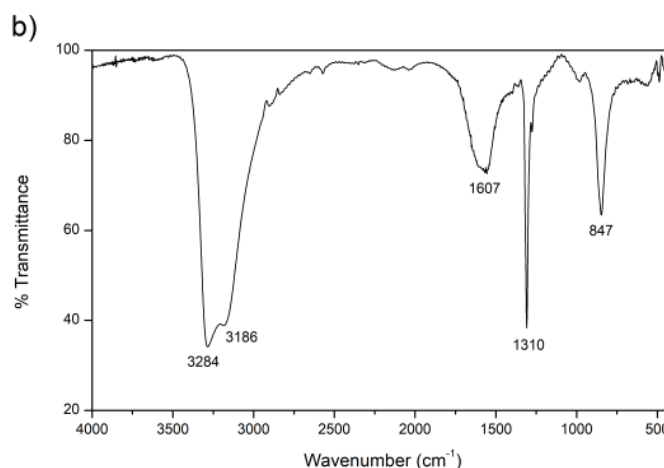
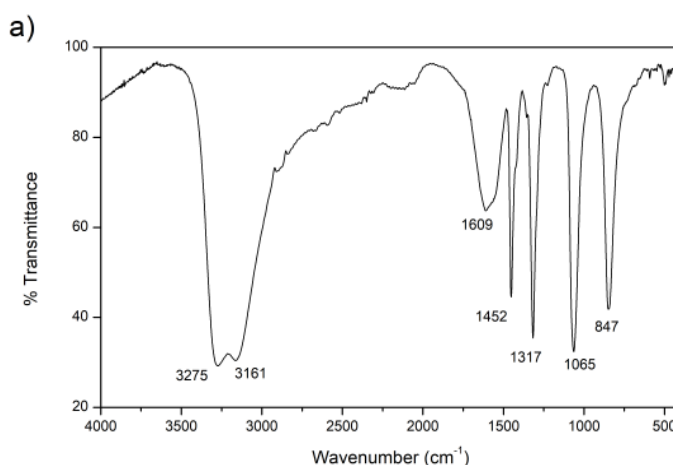


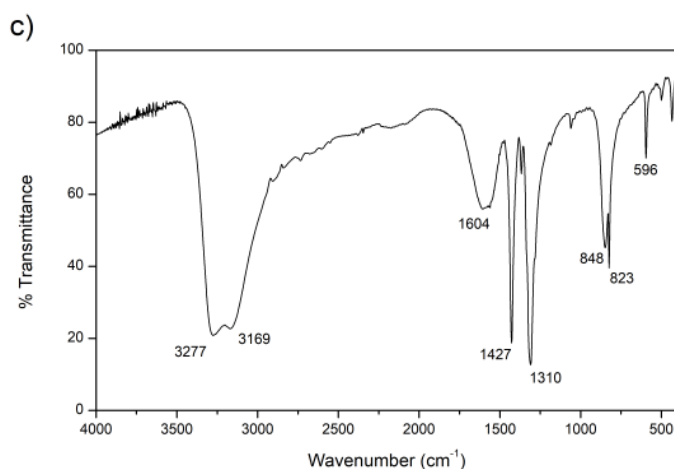
30. Applications of infrared spectroscopy to coordination chemistry

Part A

Linkage isomerism is a form of isomerism in which coordination compounds have the same composition but differ in the ligand connectivity to a metal. It can be observed in complexes in which the ligands have more than one donor atom, such as pseudohalogens or NO_2^- .

Reaction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ with NaNO_2 yields two complexes of general formula $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$. These two complexes differ in the mode of coordination of the NO_2^- anion (nitro: $-\text{NO}_2$ and nitrito: $-\text{ONO}$). The FTIR spectra of the starting material and two products are shown in figures a-c.





(a) **How many bands** are expected for the NO_2^- ion and **how are** they affected by coordination? Consider both nitro and nitrito isomers.

(b) **Which spectrum** corresponds to which of the cobalt complexes mentioned above?

Part B

Metal carbonyls are coordination complexes of transition metals with CO as a ligand. Their properties have been extensively studied as they are useful in organic synthesis and as catalyst precursors, and more recently, because of their potential in cancer therapy.

Several octahedral complexes, $[\text{M}(\text{CO})_6]^{x+}$, are known, in which the total charge depends on the metal. These can be used as precursors in the synthesis of heteroleptic complexes for different applications. IR spectroscopy enables analysis of the final product and can determine if the second ligand is bound to the metal.

(c) **How many** stretching bands are expected in the FTIR spectrum of CO and $[\text{M}(\text{CO})_6]^{x+}$?

Partial ligand substitution can lead to the formation of complexes such as $[\text{M}(\text{CO})_4\text{L}_2]^{x+}$, where L is monodentate ligand.

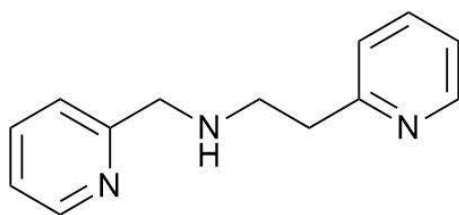
(d) **State** the type and number of possible isomers in complexes of type $[\text{M}(\text{CO})_4\text{L}_2]^{x+}$.



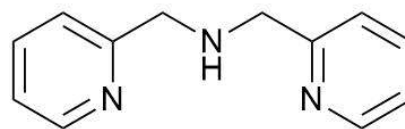
(e) The FTIR spectra of $[M(CO)_4L_2]^{x+}$ isomers show different numbers of bands in the region close to 2100 cm^{-1} . **How** would you explain this observation?

Part C

Pyridylalkyl-amine complexes became relevant as versatile platforms for several catalytic transformations, for instance, serving as models of O_2 activating metalloproteins. By treatment of a solution of $Co(ClO_4)_2$ in acetonitrile with two equivalents of pyridylalkyl-amine ligands, mononuclear complexes can be obtained rapidly in good yield. For the ligand pepma the product is a pink solid (**A**) and for bpma, a purple solid (**B**) is formed.



pepma



bpma

Infrared spectra of both compounds show very strong absorption bands around 1100 cm^{-1} . Furthermore, a medium intensity band at 3292 cm^{-1} and 3185 cm^{-1} was observed for **A** and **B** respectively. Their magnetic properties were studied, with both complexes having a value of $\mu \approx 4.0\text{ BM}$.

(f) **What** are the molecular formulae of compounds **A** and **B**? **Draw** all possible isomers of compound **A**, ignore the enantiomers of chiral structures.

(g) **Draw** the corresponding d-orbital splitting diagram and **write** down the electron configuration of the metal ion in these complexes.

(h) **Assign** the infrared bands at 1100 cm^{-1} , 3292 cm^{-1} , and 3185 cm^{-1} .

Both complexes are quite sensitive to air. Complex **A** shows reactivity to oxygen even in the solid state, as it gradually converts to an orange solid **C**. Complex **B** reacts only in solution, changing its colour to pale yellow due to the formation of compound **D**. The nature of **C** and **D** was studied through elemental analysis,



infrared spectroscopy, and magnetic studies. Both the elemental analysis and magnetic moment of complex **C** are almost the same as those of compound **A**. In the infrared spectrum of **C** an additional band at 1643 cm^{-1} was observed. The elemental analysis of **D** is significantly different from that of **B**. Compound **D** is diamagnetic.

(i) Based on this additional information, **propose** the molecular structures of compounds **C** and **D**.



Preface

Screens

At IChO 2025, students will have a screen on their desk to view the question paper. This will be the case for both the theoretical exam and the practical exam. In both exams, only the answer sheets will be printed. The desk space will be sufficiently large to allow plenty of room for students to work during both exams. You may want to practice viewing the questions on a screen during your national selection exams and training, particularly for practical work, so that students are used to this arrangement. We will provide a demo server in June 2025 for all the participating countries with the exact Examviewer software intended to be used for the ICHO 2025.



Advanced fields and standard procedures

We have written a standard procedure for each of the three advanced fields for IChO 2025: 1. Vacuum filtration; 2. Thin layer chromatography; 3. Use of a micropipette. Students are expected to learn how to perform these procedures during their training. In the final practical exam, if these procedures appear, **detailed instructions for how to perform them will not be provided**. We will only provide specific information related to the particular problem.



Safety information

In designing these Preparatory Problems we have tried as far as possible to use chemicals that are safe if handled correctly. A table of the Globally Harmonised System (GHS) hazard codes is provided for all chemicals used at the end of each experiment. This is intended as a reference only. There is no guarantee that the information provided is perfect or complete. These lists do not replace the need to comply with local regulations and the safety information provided by the actual suppliers of the chemicals.

IChO Regulation 12-3 states the following:

The use of acutely toxic substances (GHS hazard statement H300, H310, H330) is strictly forbidden. The use of toxic substances is not recommended but may be allowed if special precautions are taken. Substances with GHS hazard statements H340, H350, H360 (proven mutagens, carcinogens, and teratogens) must not be used under any circumstances (see Appendix B for definitions of these categories).

No chemicals with these hazard statements will be used at IChO 2025. In these Preparatory Problems there are some instances where it is difficult to find a suitable replacement without making the experiment impossible to perform. Mentors are welcome to adapt these procedures in line with local regulations and preferences of students. For example, these chemicals could be handled only in a fumehood, these parts of the task could be performed by mentors, or a substitute made if possible.



P1. Qualitative analysis of organic compounds

Equipment:

Item	Quantity
Nitrile gloves (S, M, L)	1
Paper tissues	1 pack
Test tube rack	1
Glass test tubes, 15 cm ³	25
Rubber stopper for the test tubes	1
Pasteur pipettes	15
Hot plate	1
Beaker (for water bath)	1
Permanent marker	1
Container for liquid waste, 1 dm ³	1



Chemicals:

Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	–	500 cm ³ (can be refilled without penalty)	Wash bottle, 500 cm ³	H ₂ O dist.
15 unknown solutions	Aqueous solutions	5%	10 cm ³	Vials, 15 cm ³	A1–A5, B1–B5, C1–C5
Copper sulfate	Aqueous solution	5%	10 cm ³	Glass dropping bottle, 30 cm ³	CuSO ₄ , 5%
Sodium hydroxide	Aqueous solution	5%	20 cm ³	Glass dropping bottle, 30 cm ³	NaOH, 5%
Potassium permanganate	Aqueous solution	1%	10 cm ³	Glass dropping bottle, 30 cm ³	KMnO ₄ , 1%,
Sulfuric acid	Aqueous solution	5%	10 cm ³	Glass dropping bottle, 30 cm ³	H ₂ SO ₄ , 5%
Sodium nitrite	Aqueous solution	5%	10 cm ³	Glass dropping bottle, 30 cm ³	NaNO ₂ , 5%



Part A: Identification using $\text{Cu}(\text{OH})_2$

Vials **A1–A5** contain aqueous solutions of the following organic compounds:

- Glucose
- Glycine (aminoethanoic acid)
- Oxalic acid (ethanedioic acid)
- Formic acid (methanoic acid)
- Acetone (propanone)

Your task is to identify the content of each vial by performing reactions with $\text{Cu}(\text{OH})_2$. You can prepare it by mixing CuSO_4 (5%) and NaOH (5%). You may also use the water bath for heating.

1. **Fill in** the table with your observations and identification results:

Vial	A1	A2	A3	A4	A5
Observations					
Compound					

2. **Write down** the chemical reactions that occurred during the identification. **Use** structural formulae for the organic compounds.



Compound	Reaction(s)
Glucose	
Glycine	
Oxalic acid	
Formic acid	
Acetone	

Part B: Identification using KMnO_4

Vials **B1–B5** contain aqueous solutions of the following organic compounds:

- Propan-2-ol
- Maleic acid (*cis*-butenedioic acid)
- Sodium formate (sodium methanoate) (solution additionally contains 5% NaOH)
- Oxalic acid (solution additionally contains 5% H_2SO_4)
- Phenol

Your task is to identify the content of each vial by performing reactions with KMnO_4 (1%). You may also use the water bath for heating.



1. **Fill in** the table with your observations and identification results:

Vial	B1	B2	B3	B4	B5
Observations					
Compound					

2. **Write down** the chemical reactions that occurred during the identification. Use structural formulae for the organic compounds.

Compound	Reaction(s)
Propan-2-ol	
Maleic acid	
Sodium formate (+NaOH)	
Oxalic acid (+H ₂ SO ₄)	
Phenol	



Part C: Identification using an acid, a base and a nitrite

Vials **C1–C5** contain aqueous solutions of the following organic compounds:

- Chloral hydrate (2,2,2-trichloroethane-1,1-diol)
- Glycine hydrochloride
- Sodium benzoate
- Aniline hydrochloride
- Acetamide (ethanamide)

Your task is to identify the content of each vial by performing reactions with the following reagents: (i) H_2SO_4 (5%); (ii) NaOH (5%); (iii) NaNO_2 (5%). You may also use the water bath for heating.

1. **Fill in** the table with your observations and identification results:

Vial	C1	C2	C3	C4	C5
Observations with H_2SO_4					
Observations with NaOH					
Observations with NaNO_2					
Compound					

2. **Write down** the chemical reactions that occurred during the identification. Use structural formulae for the organic compounds.



Compound	Reaction(s)
Chloral hydrate	
Glycine hydrochloride	
Sodium benzoate	
Aniline hydrochloride	
Acetamide	

GHS codes

Please note that the table of Globally Harmonized System (GHS) hazard codes provided for the chemicals used in these experiments is intended as a reference only. There is no guarantee that the information provided is perfect or complete. The list does not replace the need for professional attention to local regulations and the safety information provided by the actual suppliers of the chemicals.



Chemical	GHS Hazard Code(s)
D-(+)-Glucose	no hazard
Glycine	no hazard
Oxalic acid	H302+H312, H318
Formic acid	H226, H302, H314, H331
Acetone	H225, H319, H336
Copper sulfate pentahydrate	H302, H318, H410
Sodium hydroxide	H290, H314
Propan-2-ol	H225, H319, H336
Maleic acid	H302+H312, H314, H317, H335
Sodium formate	no hazard
Phenol	H301+H311+H331, H314, H341, H373, H411
Potassium permanganate	H272, H302, H314, H361d, H373, H410
Chloral hydrate	H301, H315, H319
Glycine hydrochloride	H314
Sodium benzoate	H319
Aniline hydrochloride	H301+H311+H331, H317, H318, H341, H351, H372, H410
Acetamide	H351
Sulfuric acid	H290, H314
Sodium nitrite	H272, H301, H319, H400



P2. Sørensen formol titration

Equipment:

Item	Quantity
Nitrile gloves (S, M, L)	1
Paper tissues	1 pack
Laboratory stand with a burette clamp	1
Burette, 25.00 cm ³	1
Small funnel (to fill the burette)	1
Bulb (Mohr) pipette, 5.00 cm ³	1
Bulb (Mohr) pipette, 10.00 cm ³	1
Pipette filler	1
Erlenmeyer flask, 200 cm ³	3
Graduated cylinder, 10.0 cm ³	1
Volumetric flask, 100.0 cm ³	1
Funnel (to transfer the solid or solution into the volumetric flask)	1



Graduated Pasteur pipette	1
Glass beaker, 50 cm ³	2
Container for liquid waste, 1 dm ³	1

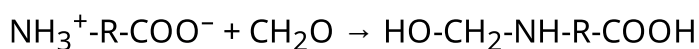
Chemicals:

Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	–	500 cm ³ (can be refilled without penalty)	Wash bottle, 500 cm ³	H ₂ O dist.
Sodium hydroxide	Aqueous solution	To be determined	200 cm ³	Glass bottle with a screw cap, 250 cm ³	NaOH
Ammonium chloride	Aqueous solution	0.1000 M	50 cm ³	Glass bottle with a screw cap, 50 cm ³	NH ₄ Cl, 0.1000 M



Phenolphthalein	Ethanol solution	1%	10 cm ³	Glass dropping bottle, 30 cm ³	Phenolphthalein
Formaldehyde	Aqueous solution	37%, neutralised with NaOH	200 cm ³	Glass bottle with a screw cap, 250 cm ³	Formalin
Amino acids mixture	Solid	Composition to be determined	Exact mass indicated on the label (ca. 1 g)	Glass beaker, 50 cm ³	AA1 + AA2, X.XXXX g

After hydrolysis, proteins form a complex mixture of amino acids. To determine the total concentration of amino acids in the sample, a formol titration, invented by a Danish chemist S. P. L. Sørensen, can be used. In this method, formaldehyde (methanal) is first added to react with the amino groups:

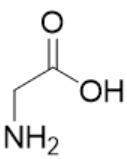
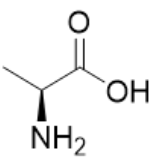
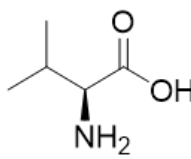
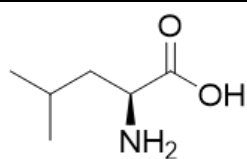
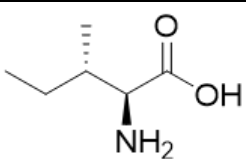
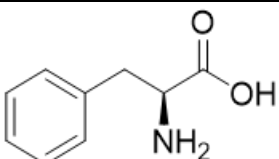


(or $\text{CH}_2=\text{N-R-COOH}$, $(\text{HO-CH}_2)_2\text{N-R-COOH}$, $\text{HOOC-R-NH-CH}_2\text{-NH-R-COOH}$, etc.)

The remaining carboxylic group is then titrated with the base.

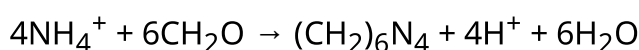
In this problem, you will need to determine the composition of a mixture prepared from two of the following amino acids: Gly, Ala, Val, Leu, Ile, Phe. The two amino acids present in your sample are indicated on the beaker.



 Glycine (Gly) $\text{C}_2\text{H}_5\text{NO}_2$ $M_r = 75.07$	 L-Alanine (Ala) $\text{C}_3\text{H}_7\text{NO}_2$ $M_r = 89.09$	 L-Valine (Val) $\text{C}_5\text{H}_{11}\text{NO}_2$ $M_r = 117.1$
 L-Leucine (Leu) $\text{C}_6\text{H}_{13}\text{NO}_2$ $M_r = 131.2$	 L-Isoleucine (Ile) $\text{C}_6\text{H}_{13}\text{NO}_2$ $M_r = 131.2$	 L-Phenylalanine (Phe) $\text{C}_9\text{H}_{11}\text{NO}_2$ $M_r = 165.2$

Step 1. Standardisation of NaOH with NH_4Cl

When ammonium salts react with formaldehyde, hexamethylenetetramine is formed according to the reaction:



The liberated protons can be titrated with the base.

Procedure:

1. **Fill** the burette with NaOH solution, using a funnel and a beaker.
2. To the Erlenmeyer flask **add**:
 - 5.00 cm^3 of NH_4Cl solution using a bulb (Mohr) pipette;
 - 3 drops of phenolphthalein solution using a dropper;
 - 5 cm^3 of neutralised formalin using a graduated cylinder.
3. **Wait** for 1–2 minutes, swirling the solution in the Erlenmeyer flask.



4. **Titrate** the mixture until there is a permanent colour change. **Record** the observed volumes in the table.

5. **Repeat** steps 2–4 as needed until you are confident of an accurate result. **Record** the observed volumes in the table. **State** your accepted final titre.

Titration number	1	2	3			
Initial burette reading, cm ³						
Final burette reading, cm ³						
Titre, cm ³						

Your accepted final titre of NaOH, $V_1 = \underline{\hspace{2cm}}$ cm³

Questions:

1. **Calculate** the concentration of the NaOH solution.

Step 2. Quantification of a Mixture of Amino Acids

Procedure:

1. **Prepare** a solution of two amino acids by dissolving the given solid mixture in distilled water in a volumetric flask.

2. To the Erlenmeyer flask **add**:

- 10.00 cm³ of the prepared amino acids solution using a bulb (Mohr) pipette;
- 3 drops of phenolphthalein solution using a dropper;
- 10 cm³ of neutralised formalin using a graduated cylinder.



3. **Wait** for 1–2 minutes, swirling the solution in the Erlenmeyer flask.
4. **Titrate** the mixture until there is a permanent colour change. **Record** the observed volumes in the table.
5. **Repeat** steps 2–4 as needed until you are confident of an accurate result. **Record** the observed volumes in the table. **State** your accepted final titre.

Titration number	1	2	3			
Initial burette reading, cm ³						
Final burette reading, cm ³						
Titre, cm ³						

Your accepted final titre of NaOH, $V_2 = \text{_____ cm}^3$

Questions:

2. **Calculate** the total amount (mol) of amino acids in the given sample.
3. Using the mass of the solid sample indicated on the label, **determine** the mass fraction of each amino acid in the initial solid mixture.

GHS codes

Please note that the table of Globally Harmonized System (GHS) hazard codes provided for the chemicals used in these experiments is intended as a reference only. There is no guarantee that the information provided is perfect or complete. The list does not replace the need for professional attention to local regulations and the safety information provided by the actual suppliers of the chemicals.



Chemical	GHS Hazard Code(s)
Sodium hydroxide	H290, H314
Ammonium chloride	H302, H319
Phenolphthalein	H315, H341, H350, H361f
Formaldehyde (37% solution)	H226, H301+H311, H314, H317, H330, H335, H341, H350, H370
Glycine	no hazard
L-Alanine	no hazard
L-Valine	no hazard
L-Leucine	no hazard
L-Isoleucine	no hazard
L-Phenylalanine	no hazard



P3. Determination of cysteine oxidation degree by two-phase titration

Equipment:

Item	Quantity
Nitrile gloves (S, M, L)	1
Paper tissues	1 pack
Laboratory stand with a burette clamp	1
Burette, 25.00 cm ³	3
Small funnel (to fill the burette)	3
Bulb (Mohr) pipette, 5.00 cm ³	2
Bulb (Mohr) pipette, 10.00 cm ³	1
Graduated pipette, 10.00 cm ³	2
Pipette filler	1
Erlenmeyer flask, 200 cm ³	3
Graduated cylinder, 10.0 cm ³	2
Graduated Pasteur pipette	4
Volumetric flask, 100.0 cm ³	2



Glass beaker, 50 cm ³	4
Container for liquid waste, 1 dm ³	1

Chemicals:

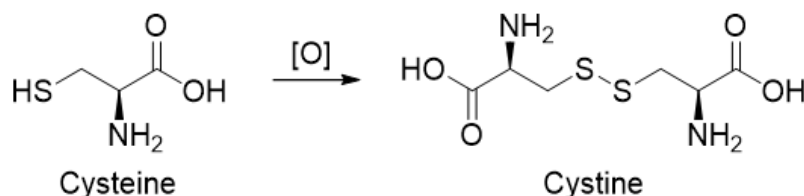
Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	–	500 cm ³ (can be refilled without penalty)	Wash bottle, 500 cm ³	H ₂ O dist.
Potassium thiocyanate	Aqueous solution	0.1000 M	100 cm ³	Glass bottle with a screw cap, 100 cm ³	KSCN, 0.1000 M
Silver nitrate	Aqueous solution	To be determined	200 cm ³	Amber glass bottle with a screw cap, 250 cm ³	AgNO ₃
Nitric acid	Aqueous solution	2 M	20 cm ³	Glass bottle with a screw cap, 50 cm ³	HNO ₃ , 2 M
Iron(III) nitrate nonahydrate	Aqueous acidic solution	2.5% in 0.1 M HNO ₃	10 cm ³	Glass dropping bottle, 30 cm ³	Fe(NO ₃) ₃ ·9H ₂ O, 2.5%



Sodium chloride	Aqueous solution	0.1000 M	50 cm ³	Glass bottle with a screw cap, 50 cm ³	NaCl, 0.1000 M
Dextrin	Aqueous solution	1%	10 cm ³	Glass bottle with a screw cap, 50 cm ³	Dextrin, 1%
Dichloro-fluorescein	Ethanolic-aqueous solution	0.1% in 70% ethanol	10 cm ³	Glass dropping bottle, 30 cm ³	Dichloro-fluorescein
Cysteine sample	Aqueous solution	4.0·10 ⁻⁴ M (before oxidation)	100 cm ³	Glass bottle with a screw cap, 100 cm ³	Cysteine sample
2,2'-Bipyridyl	Aqueous acidic solution	0.02 M in 0.05 M H ₂ SO ₄	20 cm ³	Glass bottle with a screw cap, 50 cm ³	2,2'-Bipyridyl, 0.02 M
Citrate buffer (pH 4.2)	Aqueous solution	0.2 M (NaH ₂ Cit + Na ₂ HCit)	50 cm ³	Glass bottle with a screw cap, 50 cm ³	Citrate buffer
Tetrabromo-phenolphthalein ethyl ester potassium salt	Ethanolic solution	0.03%	10 cm ³	Glass dropping bottle, 30 cm ³	TBPE, 0.03%
1,2-Dichloroethane	Liquid	–	20 cm ³	Glass bottle with a screw cap, 50 cm ³	1,2-Dichloroethane



Cysteine (Cys) is a natural amino acid containing an –SH group. It plays an important role in the structure of proteins, particularly due to the formation of disulfide (–S–S–) bridges. The analogous reaction of cysteine oxidation happens while storing the solution of cysteine in air, forming cystine:

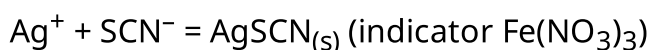


Your task is to determine the degree of cysteine oxidation using a two-phase titration with AgNO_3 .

Step 1. Standardisation of AgNO_3

To standardise the AgNO_3 solution, several methods based on precipitation reactions can be used. We encourage you to try the following methods:

Method 1. Volhard titration (this was originally a back titration for determination of Cl^-):



Procedure:

1. **Fill** the burette with KSCN solution, using a funnel and a beaker.
2. To the Erlenmeyer flask **add**:
 - 5.00 cm^3 of AgNO_3 solution using a bulb (Mohr) pipette;
 - 2 cm^3 of 2 M HNO_3 using a graduated Pasteur pipette;
 - 10 cm^3 of distilled water using a graduated cylinder;
 - 3 drops of $\text{Fe}(\text{NO}_3)_3$ solution using a dropper.
3. **Perform** the rough first titration and note the observations at the equivalence point. **Record** the observed volumes in the table.



4. **Repeat** steps 1–2 and titrate more accurately until you are confident of an accurate result. **Record** the observed volumes in the table. **State** your accepted final titre.

Titration number	1 (rough)	2	3	4		
Initial burette reading, cm ³						
Final burette reading, cm ³						
Titre, cm ³						

Your accepted final titre of KSCN, $V_1 = \text{_____ cm}^3$

Questions:

1. **Indicate** the observations at the equivalence point in the Volhard titration and **write down** the reaction responsible for them.
2. **Calculate** the concentration (c_1) of AgNO_3 solution according to the Volhard titration.

Method 2. Fajans titration (direct titration):



Procedure:

1. **Fill** the burette with AgNO_3 solution, using a funnel and a beaker.
2. To the Erlenmeyer flask **add**:
 - 5.00 cm³ of NaCl solution using a bulb (Mohr) pipette;
 - 10 cm³ of distilled water using a graduated cylinder;



- 1 cm³ of dextrin solution using a graduated Pasteur pipette;
- 3 drops of dichlorofluorescein indicator solution using a dropper.

3. **Perform** the rough first titration and note the observations at the equivalence point. **Record** the observed volumes in the table.

4. **Repeat** steps 1–2 and titrate more accurately until you are confident of an accurate result. **Record** the observed volumes in the table. **State** your accepted final titre.

Titration number	1 (rough)	2	3	4		
Initial burette reading, cm ³						
Final burette reading, cm ³						
Titre, cm ³						

Your accepted final titre of AgNO₃, $V_2 = \text{_____ cm}^3$

5. **Repeat** the titration without the addition of dextrin solution. **Note** your observations.

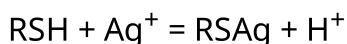
Questions (continuation):

3. **Indicate** the observation at the equivalence point in the Fajans titration and **explain** the action of the indicator.
4. **Calculate** the concentration (c_2) of AgNO₃ solution according to the Fajans titration and the average concentration ($c(\text{AgNO}_3)$) of AgNO₃ based on two methods (if you have performed both of them).
5. **Indicate** the observations for the titration without dextrin and **state** the role of dextrin in the Fajans titration.



Step 2. Quantification of Cysteine

The titration is based on the following reaction:



The analysed sample contains microquantities of cysteine. Therefore, the titrant must first be accurately diluted.

Procedure:

1. **Prepare** 100 cm³ of AgNO₃ solution diluted 200 times by a series of two dilutions using two volumetric flasks (capacity 100 cm³) and two graduated pipettes (capacity 10.00 cm³).
2. **Fill** the burette with the diluted AgNO₃ solution, using a funnel and a beaker.
3. To the Erlenmeyer flask **add**:
 - 10.00 cm³ of cysteine sample solution using a bulb (Mohr) pipette;
 - 2 cm³ of 2,2'-bipyridyl solution using a graduated Pasteur pipette;
 - 10 cm³ of citrate buffer solution using a graduated cylinder;
 - 5 drops of TBPE indicator solution using a dropper;
 - 2–3 cm³ of 1,2-dichloroethane using a graduated Pasteur pipette.
4. **Titrate** the mixture with intermittent hand shaking until the colour in the organic phase changes from faint yellow to sky blue. **Record** the observed volumes in the table.
5. **Repeat** steps 2–4 as needed until you are confident of an accurate result. **Record** the observed volumes in the table. **State** your accepted final titre.



Titration number	1	2	3			
Initial burette reading, cm ³						
Final burette reading, cm ³						
Titre, cm ³						

Your accepted final titre of diluted AgNO₃, $V_3 = \text{_____ cm}^3$

Questions (continuation):

6. **Calculate** the cysteine oxidation degree (%) in the given sample.

GHS codes

Please note that the table of Globally Harmonized System (GHS) hazard codes provided for the chemicals used in these experiments is intended as a reference only. There is no guarantee that the information provided is perfect or complete. The list does not replace the need for professional attention to local regulations and the safety information provided by the actual suppliers of the chemicals.



Chemical	GHS Hazard Code(s)
Potassium thiocyanate	H302+H312+H332, H318, H412
Silver nitrate	H272, H290, H314, H360D, H410
Nitric acid	H272, H290, H314, H331
Iron(III) nitrate nonahydrate	H314
Sodium chloride	no hazard
Dextrin	no hazard
Dichlorofluorescein	no hazard
Cysteine	no hazard
2,2'-Bipyridyl	H301+H311
Citrate buffer	H351, H373
Tetrabromophenolphthalein ethyl ester potassium salt	no hazard
1,2-Dichloroethane	H225, H302, H304, H315, H319, H331, H335, H350



P4. Synthesis and characterisation of a paramagnetic cobalt acetylacetonate complex

Part 1: Synthesis of complex A

Labware:

Item	Quantity
Shared	
Nitrile gloves (S, M, L)	3+ packs
paper tissues	Extra packs
analytical balance	1
Gouy balance	1
weighing papers	3+ packs
For each student	
hotplate with magnetic stirrer	1
magnetic stirrer bar (small)	2
Pasteur pipette	1
steel spatula	1
Buchner funnel & rubber funnel seal	1
Buchner flask	1
rubber vacuum hose	1
filter paper (Whatman-1)	3
lab stand with clamp	1
sticky label	1
50 mL glass beaker	1
100 mL glass beaker	1
10 mL graduated cylinder	1
50 mL graduated cylinder	1
glass rod	1
container for liquid waste, 1 dm ³	1
glass vial labelled as compound A	1



Chemicals:

Name	State	Concentration	Quantity	Placed in	Label
For each student					
Distilled water	Liquid	–	500 cm ³	Wash bottle, 500 cm ³	H ₂ O dist.
Sodium hydroxide	Solid		402 mg		NaOH
Acetylacetone	Liquid		1.5 cm ³		Acetylacetone
Cobalt chloride hexahydrate	Solid		1200 mg		CoCl ₂ ·6H ₂ O



Part 2: Oxidation of Complex A:

Labware:

For each student	
hotplate with magnetic stirrer	1
magnetic stirrer bar (small)	1
steel spatula	1
Pasteur pipette	1
Buchner funnel & rubber funnel seal	1
Buchner flask	1
rubber vacuum hose	1
filter paper (Whatman-1)	3
lab stand with clamp	1
sticky label	1
100 mL glass beaker	1
10 mL graduated cylinder	1
glass rod	1
container for liquid waste, 1 dm ³	1
Glass vial labelled as compound B	1



Chemicals:

Name	State	Concentration	Quantity	Placed in	Label
For each student					
Distilled water	Liquid	–	500 cm ³	Wash bottle, 500 cm ³	H ₂ O dist.
Compound A	Solid		500 mg		Compound A
Hydrogen peroxide	Solution	30% (keep refrigerated)			H ₂ O ₂ (30%)



Part 3: Characterisation

Labware:

For each student	
spectrophotometer	1
hot plate	1
50 mL volumetric flask	3
50 mL Erlenmeyer Flask	2
quartz cuvettes	5
1 mL volumetric pipette or (20-1000 μ L) micropipette	1
micropipette tips (20-1000 μ L)	15
50 mL glass beaker	1
container for liquid waste, 1 L	1



Chemicals:

Name	State	Concentration	Quantity	Placed in	Label
For each student					
Distilled water	Liquid	–	500 cm ³	Wash bottle, 500 cm ³	H ₂ O dist.
Compound A	Solid		20 mg		
Concentrated nitric acid	Liquid		5 cm ³		
HCl	Liquid	6 M	20 cm ³		
6 M HNO ₃	Liquid	6 M	5 cm ³		
Nitroso-R solution	Aqueous solution	0.1%	3 cm ³		
Sodium acetate	Aqueous solution	10%	10 cm ³		

Synthesis and characterisation of a paramagnetic cobalt acetylacetonate complex

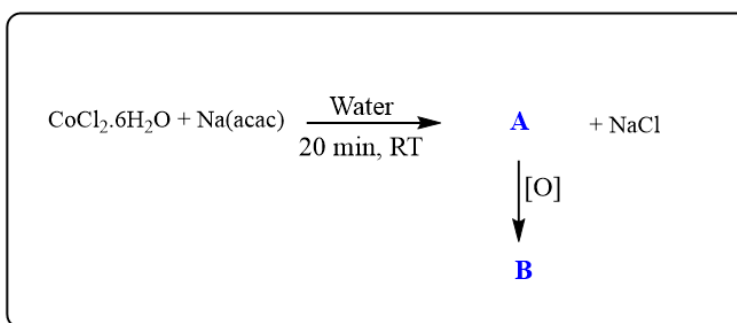
Metal acetylacetonate complexes are one of the most well known and studied classes of compounds in inorganic teaching labs. Acetylacetonate complexes can be easily obtained through the combination of an appropriate metal salt with the acetylacetonate anion under mild reaction conditions. The acetylacetonate anion can be generated in situ through deprotonation of the β -diketone, using a mild base in water or alcoholic solvent.



Acetylacetonate complexes are known for most of the metals and metalloids in the periodic table. As this class of complexes has been known for many decades, and the synthetic routes are well established, numerous studies have been conducted to investigate the application of these molecules in various fields. Not surprisingly, metal acetylacetonates have proved themselves to be useful molecules, and they play crucial roles in various chemical and industrial processes.

This task will be completed in three parts. In the first part, you will synthesise a cobalt acetylacetonate complex, which you will then oxidise in the second part. In the third part, you will characterise the complexes formed, using magnetic studies and spectroscopic methods.

Part 1: Synthesis of complex A



1. **Weigh** precisely about 0.4 g of NaOH pellets (record the weight to 4 decimal points) into a 50 mL beaker.
2. **Dissolve** the NaOH pellets in 10.0 mL distilled water (use a tiny magnetic stirrer bar).
3. **Measure** 1.00 mL of acetylacetone using a Pasteur pipette and **add drop by drop** into the NaOH solution whilst stirring. **It is recommended that you use a fumehood for this step.** If any white solid is formed during this step, add a few additional millilitres of distilled water to redissolve it.
4. **Weigh** 1.196 g (5.02 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ crystals into a 100 mL beaker.
5. **Add** 30.0 mL of deionised water.
6. **Add** a magnetic stirrer bar, and gently stir until the cobalt crystals dissolve.



7. Using a Pasteur pipette, **add dropwise** all the sodium acetylacetonate solution that you prepared in step 3.
8. A pink coloured precipitate forms.
9. **Continue stirring** the reaction mixture for 20 min at room temperature.
10. **Collect** the pink precipitate obtained using the vacuum filtration equipment (See the standard procedure given for vacuum filtration).
11. Transfer the pink precipitate into a pre-weighed glass vial labelled as Complex A.
12. Keep the glass vial containing Complex A in an oven set at 60°C for 1 hr to completely dry the sample and cool in a dry condition.

Questions:

- 1.1 **Draw** a mechanism for the deprotonation reaction of the β -diketone with NaOH.
- 1.2 Using a Gouy or Faraday balance, **record** the magnetic susceptibility of **complex A**.

(please note that use of a Gouy or Faraday balance and magnetic susceptibility measurements/magnetic moment determination will not appear at IChO 2025).

- 1.3 Given the chemical formula of **complex A** is $\text{CoO}_6\text{C}_{10}\text{H}_{18}$, determine the following parameters for **complex A**.
 - a. Molar susceptibility of this complex, χ_m : _____
 - b. Spin only effective magnetic moment, μ_{eff} : _____
 - c. Number of unpaired electrons: _____

Part 2: Oxidation of Complex A:

1. **Weigh** precisely about 0.5 g of complex **A** into a 100 mL beaker.
2. **Add** 10.0 mL of deionised water and **stir** using a magnetic stirrer bar (resulting in a pink suspension).



- Using a Pasteur pipette, **add dropwise** 6 mL of H_2O_2 (30% aqueous solution) directly into the beaker.
- An immediate colour change from pink to green can be observed.
- Turn on** the hot plate and **stir** for 20 min while keeping the temperature around 60 °C.
- Turn off** the heating and keep the resulting green solution for crystallisation overnight.
- On the next day, **filter** the reaction mixture using the vacuum filtration equipment (See the standard procedure given for vacuum filtration).
- Let** air pass through the product (green coloured crystals) for 5 min to dry it.
- Transfer** the dried product into a pre-weighed glass vial labelled as **complex B**.

Questions:

- Report** the weight of the **complex B**
- Using a Gouy or Faraday balance, **record** the magnetic susceptibility of the **complex B**.

Part 3: Characterisation

Characterisation of compound A by cobalt analysis:

Formation of a cobalt nitroso-R complex:

- Weigh** 20 mg of **complex A** into a 50 mL beaker.
- Add** 10-20 drops of conc. nitric acid and gently evaporate nearly to dryness (**in the fumehood**) over a hot plate.
- To this moist residue, **add** 12 mL of 6 M HCl and 1.5 mL of 6 M HNO_3 , and **transfer** the whole solution into a 50 mL volumetric flask and **make up to the mark** with water.
- Using a micropipette or volumetric pipette, **transfer** exactly 2.00 mL of the solution prepared in step 3 into a 50 mL Erlenmeyer flask, and **add** 8 mL of water into the flask.



- Using a hot plate, **gently boil** the solution in the flask for 3 min.
- After cooling, **add** 3.0 mL of 0.1% nitroso-R solution and 10 mL of 10% sodium acetate solution into the flask.
- Heat** the resulting solution to bring it to boiling for 1 min, and then **add** 1.0 mL of 6 M HCl.
- Heat** the resulting solution again to boiling, and allow the coloured solution formed to cool to room temperature.
- After the solution has cooled to room temperature, transfer the entire solution into a 50 mL volumetric flask and **dilute** the solution in the flask up to the mark using water.
- Measure** an absorption spectrum of this cobalt nitroso-R complex solution against the blank solution.

Preparing a blank sample:

- To a 50 mL Erlenmeyer flask, **add** 10 drops 6 M HCl and two drops of 6 M HNO₃.
- Add** 8 mL of water into the flask.
- Using a hot plate, **gently boil** the solution in the flask for 3 min.
- After cooling, **add** 3.0 mL of 0.1% nitroso-R solution and 10 mL of sodium acetate into the flask.
- Heat** the resulting solution to bring it to boiling for 1 min, and then **add** 1.0 mL of 6 M HCl.
- Heat** the resulting solution again to boiling, and allow to cool to room temperature.
- After the solution has cooled to room temperature, transfer the entire solution into a 50 mL volumetric flask, and **dilute** the solution in the flask up to the mark using water. Mark this solution as **Solution A**.
- Use** this solution as the blank solution to zero the spectrophotometer.

Absorption measurement using the UV-VIS spectrophotometer:



NB: Measure the absorbance at 500 nm ($\epsilon = 1.45 \times 10^4 \text{ cm}^{-1} \text{ l mole}^{-1}$)

Calibrate the spectrophotometer:

1. **Turn** on your spectrophotometer and allow the lamp to warm up (approximately 15 min depending on model).
2. **Fill** your cuvette with the blank reagent and **clean** the outside surface afterwards.
3. **Place** the cuvette in the spectrophotometer and **run** the blank sample.

Performing an absorption spectrum:

1. **Rinse** your cuvette two times with the cobalt nitroso-R complex solution and then **fill** it about three quarters full.
2. **Place** the cuvette in the spectrophotometer in the correct direction and close the sample holder.
3. **Collect** the absorbance spectrum of the sample by scanning over a range of wavelengths (wavelength range from 200-800 nm is standard).
4. In your spectrum, measure the absorbance at $\lambda = 500 \text{ nm}$.

Questions:

3.1 Using the Beer-Lambert Law, **determine the concentration of cobalt in Solution A.**

3.2 Using the magnetic data, provide the following information for **compound A**:

- Ground spin state: _____
- Oxidation state of the Co centre: _____
- Most probable geometry: _____
- Draw the structure of the complex
- Draw the possible d orbital splitting for this complex and fill in the electrons.

3.3 Using the magnetic data, provide the following information for the **compound B**.

- Ground spin state: _____



- Oxidation state of the Co centre: _____
- Most probable geometry: _____
- Draw the possible d orbital splitting for this complex and fill in the electrons.

3.4 From your observations, **how** does oxidation at the metal centre affect the magnetic behaviour and spin state of **compound A**?

GHS codes

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Chemical	GHS Hazard Code
Deionised water	No hazard
Sodium hydroxide	H290, H314
Acetylacetone	H226, H302, H311+H331
Cobalt chloride hexahydrate	H302, H317, H334, H341
Hydrogen peroxide 30%	H271, H302, H314+H318, H333
conc. Nitric acid (HNO ₃)	H314, H331, H290
6 M HCl	H290, H314, H335
6 M HNO ₃	H272, H290, H314, H318
1% Nitroso-R solution	H302+H312+H332
Sodium acetate	Not classified



P5. Never late with thiosulfate

*"Studying reaction kinetics provides insight into the mechanism,
revealing the intricate steps that convert reactants into products."*

Linus Pauling

Equipment:

Item	Quantity
Nitrile gloves (S, M, L)	1
Paper tissues	1 pack
1.5 mL or 2 mL Eppendorf tubes	15 tubes
Microsynthesis plate	1
Micropipette (P-200)	1
Micropipette (P-2000)	1
Micropipette types	15
Stopwatch or clock	1
Container for liquid waste, 1 dm ³	1

Chemicals:



Name	State	Concentration	Quantity	Placed in	Label
Distilled water	Liquid	–	50 cm ³ (can be refilled without penalty)	Wash bottle, 500 cm ³	H ₂ O dist.
Hydrogen peroxide	Liquid	0.2 M	20 cm ³		H ₂ O ₂ (0.2 M)
Starch solution	Liquid	2% (w/v)	20 cm ³		starch solution
Sulfuric acid	Liquid	1M	20 cm ³		H ₂ SO ₄ (1M)
Sodium thiosulfate	Liquid	0.01 M	20 cm ³		Na ₂ S ₂ O ₃ (0.01M)
Potassium iodide	Liquid	0.1 M	20 cm ³		KI (0.1M)

Introduction to clock reactions

Clock reactions are chemical reactions that exhibit a significant delay before a noticeable change occurs, such as a colour change or precipitate formation. This delay is due to a build-up of intermediate products that only become visually apparent once a specific concentration threshold is reached. The time taken for this change to occur can be precisely measured and is influenced by factors such as reactant concentrations and temperature. They are frequently used to demonstrate the principles of reaction kinetics and chemical dynamics.

The clock reaction between H₂O₂ and KI, in the presence of S₂O₃²⁻, is the classical clock reaction. The reaction product iodine, initially formed slowly, reacts with



thiosulfate ($\text{S}_2\text{O}_3^{2-}$) until it's depleted. Then, a sudden appearance of a dark blue starch-iodine complex signals the completion of the thiosulfate reaction.

Objective

In this experiment, we will build a chemical clock: a series of solutions which consequently change colour minute after minute and that is why serve as a clock and this clock we will use for next kinetics studies.

Two clocks will be prepared: first clock will be made using Eppendorf tubes and the second clock will be made via microsynthesis plate which will reduce the reaction scale 2-3 times more.

For this, we will conduct a series of iodine clock reactions using H_2O_2 and KI to illustrate reaction kinetics, where the endpoint is indicated by a colour change due to starch-iodine complex formation.

Preliminary questions

- (a) Write balanced equations of both reactions involved in this chemical clock process.
- (b) Why do we need acid conditions for this solution?
- (c) Which indicator is possible to use instead of starch?

Protocol

Step 1: Reaction Test

1. Preparation of three test tubes:

For each tube, we prepare 0.9 mL solution in the following way:

Add varying volumes of 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$: 50, 75 and 100 μL using the P-200 micropipette

Add 50 μL (0.05 mL) of 1 M H_2SO_4 solution using the P-200 micropipette.

Add 100 μL (0.10 mL) of 0.1 M KI solution using the P-200 micropipette.

Add 25 μL of the 2% (w/v) starch solution



Fill the tube up to 0.9 mL with distilled water using the P-2000 micropipette.

2. Test Reaction Timing:

When these 3 tubes are ready, close the tubes and shake them. Then, add 100 μL (0.10 mL) of 0.2 M H_2O_2 to each solution and start the timer to measure colour change time with a precision of 1 second. You could add an arbitrary 2-3 seconds correction to each next tube, as it is not possible to perform simultaneously. However, this correction is not as necessary, as this test is a rough estimation of the best solution.

You should find the condition to obtain the solution which has colour change in 100–200 seconds. If in your conditions no one of these solutions has a given time, adjust the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution basing on the obtained results. If several solutions correspond to the given range, use the latest solution.

The volume of $\text{Na}_2\text{S}_2\text{O}_3$ for the best tube will be used in the whole our experiment.

Step 2: Preparation of the 4 minutes Chemical Clock

1. Preparation of 4 Eppendorf tubes:

For each tube, add:

- § The volume that you found in previous step of 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution
- § 50 μL (0.05 mL) of 1 M H_2SO_4 .
- § In different tubes put 300, 150, 100, 75 of 0.1 M KI solution, respecting this order.
- Add 25 μL of the 2% (w/v) starch solution
- § Fill with water up to 0.9 mL

As before, first, close and shake these 4 tubes. Add 100 μL (0.10 mL) of 0.2 M H_2O_2 for first 4 tubes. Add the solutions to the first 4 tubes (order is the decreasing volume of KI) respecting the same time interval (3-5 seconds, without using clock, just counting by yourself).

Time Differences verification :

Using the clock completely (4 minutes), ensure the timing differences of colouration of the next solution are within a 10% margin, and it happens each 25–70 seconds. Yours

obtained time change we will label as the “chemical minute”.

Conclude which the reaction order for the KI reactant.

Step 3: Preparation of the 4 minutes Chemical Clock on the plate.

Now, the idea is to prepare micro-clock using the microsynthesis plate where the volume of the well is 400 μL (0.40 mL).

Before, the total volume solution in tube was 1.0 mL and now we should reduce it to 0.4mL. Using the adjustments for step 2 step (i.e. reducing volumes 2.5 times), repeat the step 2 using the microsynthesis plate. However, for this experiment is not possible to shake before addition of H_2O_2 .

Compare both clocks and explain, why one of them is better than another.

Step 4. Main part

Now, choosing the clock which works better, we can use it for two short experiments **A** and **B**.

As possibly, we will need 8 "chemical minutes" for the main part, prepare two sets of 4 minutes clocks without adding

H_2O_2 solution as it should be added at the moment when we will need to launch the clock (first four tubes and then last four tubes).

A: Order of H_2O_2 Reactant

1. Prepare 2 new tubes (A1 and A2):

For each tube, add:

The same volume of 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution

50 μL (0.05 mL) of 1 M H_2SO_4 .

100 μL (0.10 mL) of 0.1 M KI.

Add 25 μL of the 2% (w/v) starch solution

Fill with water up to 0.95 mL



So, from this moment you could lunch first 4 minutes clock in the same way as before. Then launch **A1** tube (by adding 0.05 mL of H_2O_2 as in the previous experiment) when the second clock tube change colour (i.e. second “chemical minute”). In the same way launch **A2** tube on the third “chemical minute”.

You will see if it would be necessary to activate the second 4 minutes clock. If you will use second clock then keep it for the next experiment (B).

Note at what chemical minute the colour change is observed and from this observation find the reaction order of H_2O_2 .

B: Determination of H_2O_2 concentration

1. Prepare 2 new tubes (B1 and B2):

For each tube, add:

The same volume of 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution

50 μL (0.05 mL) of 1 M H_2SO_4 .

100 μL (0.10 mL) of 0.1 M KI.

Add 25 μL of the 2% (w/v) starch solution

Fill with water up to 0.95 mL

So, from this moment you could lunch first 4 minutes clock in the same way as before. Then launch **B1** tube (by adding 0.05 mL of H_2O_2 with new concentration) when the second clock tube change colour. In the same way launch **B2** tube on the third “chemical minute”.

You will see if it would be necessary to activate the second part of your clock.

Note at what chemical minute the colour change is observed for each solution and then find the concentration of the H_2O_2 solution.

GHS codes



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Chemical	GHS Hazard Code
H ₂ O ₂ (0.2 M solution)	H271, H302, H314, H335
Starch Solution (2% w/v)	No hazard
H ₂ SO ₄ (1 M solution)	H314
Na ₂ S ₂ O ₃ (0.01 M solution)	No hazard
KI (0.1 M solution)	H372

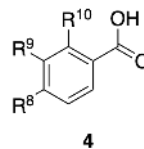
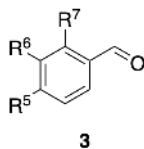
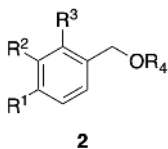
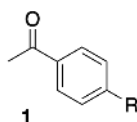


P6. To condense or not to condense?

To condense or not to condense, that is the question: whether you will differentiate between two starting materials by the means of their reactions or not.

You have three out of four compounds **1-4**. Compound **1** is known and labelled as “**1**”, while the other two chemicals are two out of three possible compounds **2-4**, and they are labelled as “**A**” and “**B**”. You will perform a condensation reaction with them if possible.

Substituents R and Rⁿ do not interfere with any possible reaction and do not produce any side processes within the conditions used.



Experimental procedure

Equipment:



Item	Quantity
Nitrile gloves (S, M, L)	1
Paper tissues	1 pack
Graduated cylinder (10 ml)	1
Pasteur pipettes	20
Water bath	1
Stir plate	1
Vials (20 ml)	3
Vial (2 ml)	10
Stir bars	3
Permanent marker	1
Glass capillaries/pipette tips	8
TLC plate with fluorescent indicator	3
Forceps	1
TLC chamber	1
Pencil	1
Ruler	1
254 nm UV lamp	1 (for the group of students)



small steel spatula	1
Buchner funnel & rubber funnel seal	1
Buchner flask	1
rubber vacuum hose	1
filter paper	1
lab stand with clamp	1
pH indicator paper	5



Chemicals:

Name	State	Concentration	Quantity (per student)	Placed in	Label
Chemical 1		pure	2.5 mmol	vial	1.A
Chemical 1		pure	2.5 mmol	vial	1.B
Chemical A		Solution in EtOH (3-5 ml)	2.8 mmol	vial	A
Chemical B		Solution in EtOH (3-5 ml)	2.8 mmol	vial	B
EtOAc	liquid	-	50 ml	bottle	EtOAc
EtOH	liquid	-	50 ml	bottle	EtOH
H ₂ O	liquid	-	250 ml	bottle	H ₂ O
NaOH	solid	-	0.15 g 0.15 g 0.1 g	vial	NaOH A NaOH B NaOH C
KMnO ₄	solution	0.01M	1 ml	Common reagent bottle	KMnO ₄
nitromethane	liquid	-	0.5 ml	vial	nitromethane



Part A: Condensation reaction with compounds A and B

Warning: the procedure must be done cautiously with safety goggles and gloves. Sodium hydroxide is dangerous for eyes, and it may cause partial or complete blindness if it is in contact with eyes in both liquid and solid form.

1. **Prepare** the samples for TLC analysis. For this **add** one drop of compound **1** into the 2 ml vial and **label** the vial as "**1**". **Add** EtOAc (1 mL) to the vial.
2. **Repeat** the process for compounds **A** and **B**. For them you need to add less EtOAc (0.2 ml).
3. **Take** a reaction vial (20 ml). **Label** it as **A**.
4. **Add** all the NaOH labelled as "NaOH A" and water (1.5 mL) to the reaction vial containing a stir bar. Stir the solution for 1 min.
5. **Add** EtOH (1 mL). Stir until the solution is homogeneous.
6. **Cool** the solution with a water bath. For the cooling bath use room temperature water (50% of the bath volume) and ice (50% of the volume).
7. **Stir** the solution in the cooling bath for 3 mins.
8. **Add** all the compound **1.A** in one portion.
9. **Add** the solution of compound **A** dropwise via pipette (add one drop per second) with vigorous stirring.
10. **Note** the time after the addition is completed, remove the cooling bath and continue the stirring.
11. **Repeat** the steps 3-10 but with the compounds **1.B** and **B** instead of **1.A** and **A**.
12. **Check** each reaction TLC after 30 mins.
13. For this prepare the TLC plate. Mark the starting line and three spots labelled (1, R, A) at equal distance.
14. **Prepare** a TLC chamber with EtOAc:Hex = 1:9 as eluent.
15. **Take** one drop of reaction mixture A and **add** it to a new 2 ml vial. **Label** the vial as AR. Add EtOAc (0.2 ml) to this vial, close it and gently shake to mix the solution.
16. **Load** the samples on the prepared TLC plate.
17. **Run** the TLC.
18. **Check** the TLC under UV visualization and **circle** all visible spots.
19. **Q1: Choose** the appropriate answer about the observations below.



Is it possible to distinguish reaction completeness by this TLC?	Yes/No
Is it better to use another eluent mixture?	Yes/No
Is the reaction complete?	Yes/No/Unknown
Is there a product formation observed by TLC?	Yes/No/Unknown
Is there any visible sign of the reaction (gas evolution or precipitate formation)?	Yes/No

20. **Repeat** the steps 13-18 for the reaction mixture B.

21. **Q2:** Choose the appropriate answer about the observations below.

Is it possible to distinguish reaction completeness by this TLC?	Yes/No
Is it better to use another eluent mixture?	Yes/No
Is the reaction complete?	Yes/No/Unknown
Is there a product formation observed by TLC?	Yes/No/Unknown
Is there any visible sign of the reaction (gas evolution or precipitate formation)?	Yes/No

22. **Stir** the reaction mixtures for additional 15 mins and meanwhile **answer** the questions below.

23. **Q3:** According to the observations, **choose** the correct structures for compounds **A** and **B** in the table below (write A or B in the appropriate place).

2:	3:	4:
----	----	----

24. **Q4:** Which property/properties of compounds **2-4** allowed you to differentiate between them? **Choose** all that applies.

- A. Magnetic properties.
- B. Red-Ox properties.
- C. Acid-base properties.
- D. Electrochemical properties.
- E. Photophysical properties.

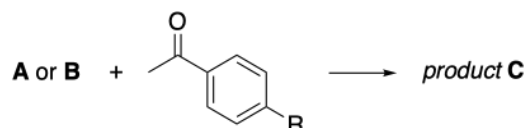
25. After additional 15 mins has finished, **add** 10 ml of water to each reaction mixture.



26. **Filter** the precipitate using vacuum filtration. **Wash** the obtained compound with water until almost neutral pH is achieved; check the pH of a filtrate occasionally using indicator paper.

27. **Dry** the product in vacuo. You may use crude undried product for further steps.

Part B: product analysis



1. **Add** one small spatula (~20 mg) of the isolated product **C** to a new 2 ml vial.
2. **Add** 1 ml of KMnO_4 solution (0.01M) to this vial.
3. **Shake** the vial vigorously and **observe** the changes.
4. **Q5: Answer** the questions below and **draw** the structure of product **C**. Assume that all the substituents (R and R^n) are hydrogens for the product structure.

Was there a gas evolution?	Yes/No
Was there a precipitate formation?	Yes/No
Was there a colour change?	Yes/No
Is it possible to detect this chemical on TLC by permanganate stain visualization instead of UV visualization?	Yes/No
Draw the structure of product C	

Part C: more condensations?

1. **Prepare** a reference sample of nitromethane and the isolated product **C**. For this take two 2 ml vials, label them as N (nitromethane) and C (product **C**). Take a sample of each compound and place it to a labelled vial. **Add** EtOAc (1 ml) to each vial.



2. **Take** a reaction vial (20 ml), place a stir bar there. **Add** 10 small spatulas (~200 mg) of the isolated product **C** to the vial.
3. **Add** EtOH (4 ml) and nitromethane (0.5 ml), start the stirring.
4. To the 2 ml vial labeled as "NaOH C" **add** H₂O (1 ml). **Mix** the solution until the solid is dissolved.
5. **Add** solution of NaOH dropwise (1 drop per second) to the reaction mixture.
6. **Stir** the reaction mixture for 10 mins.
7. **Check** the TLC of the reaction mixture using the following instructions.
8. **Take** 10 drops of the reaction mixture, **add** to a separate 2 ml vial, **add** EtOAc (0.2 ml) there.
9. **Prepare** the TLC plate. **Mark** the starting line and three spots labelled (C, R, N) at equal distance.
10. **Load** the samples and **run** the TLC. Use the same TLC chamber with EtOAc:Hex = 1:9 as eluent.
11. **Visualize** the TLC plate using the UV lamp. **Circle** all the visible spots.
12. **Q6: Draw** a possible structure of product **D** that can be formed in the reaction performed. Assume that all the substituents (R and Rⁿ) are hydrogens for the product structure.

13. **Q7: Choose** the appropriate answer about the observations below.

Is it possible to distinguish reaction completeness by this TLC?	Yes/No
Is it better to use another eluent mixture?	Yes/No
Is the reaction complete?	Yes/No/Unknown
Is there a product D formation observed by TLC?	Yes/No/Unknown

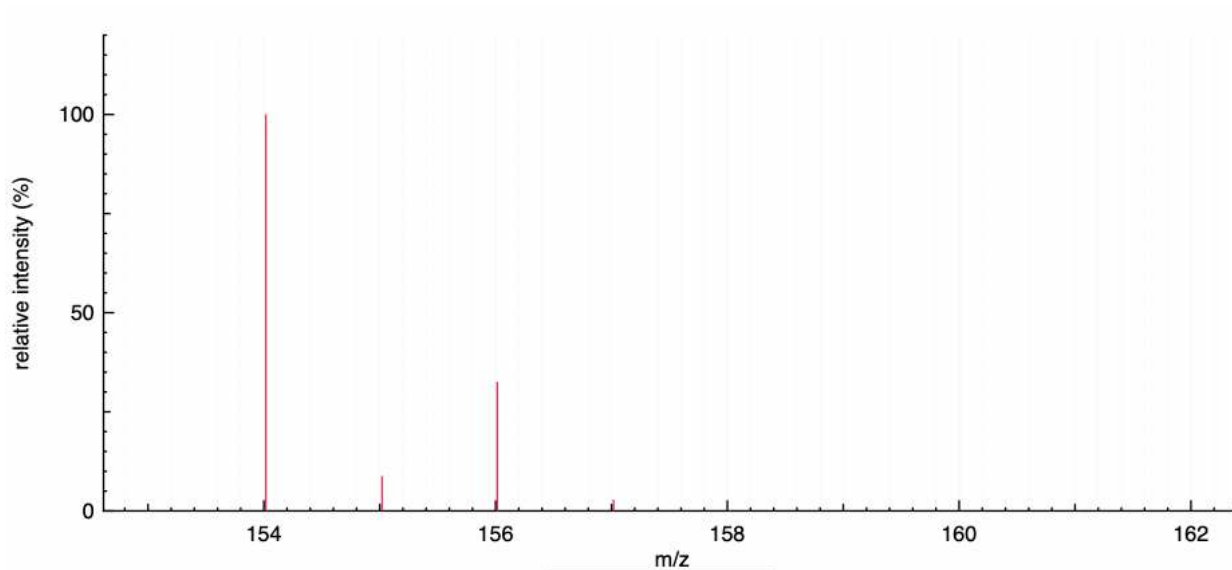
Part D: what are the products?

Below mass spectra are presented for compound **1** and possible product **D**.

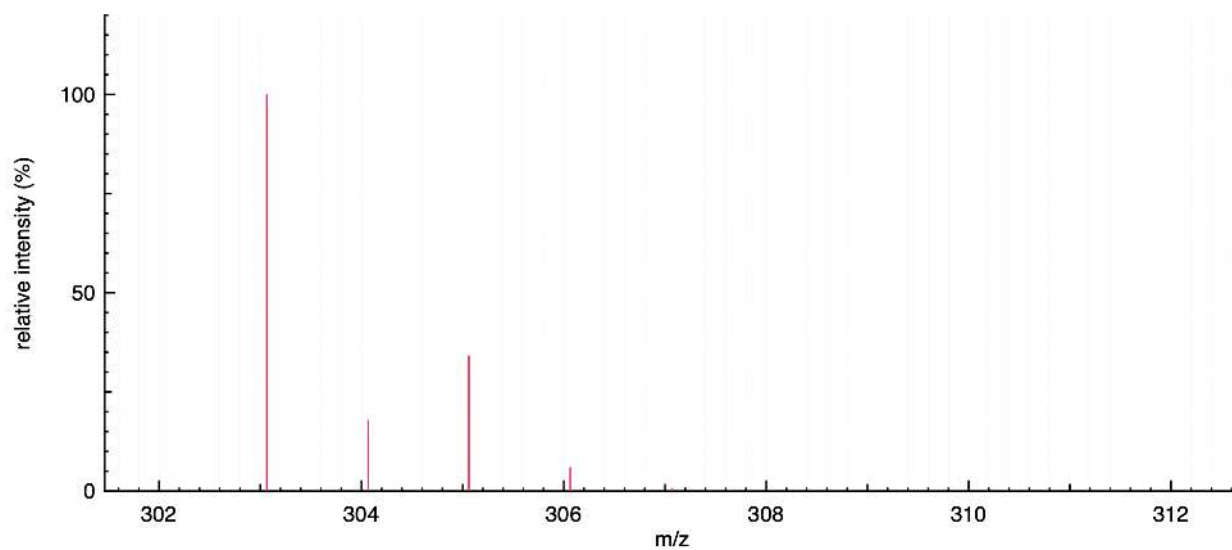


Q8: Draw the structures of compounds **1** and **D** that fit the presented spectra.

MS of **1**



MS of product **D**





GHS codes

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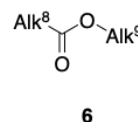
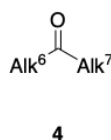
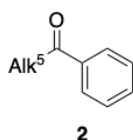
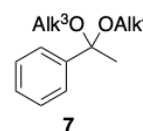
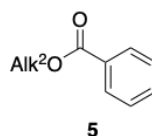
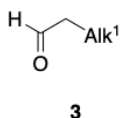
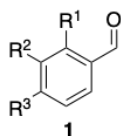
Chemical	GHG code(s)
Chemical 1	
Chemical A	
Chemical B	
EtOH	H225, H319
EtOAc	H225, H319, H319
Hexane	H225, H304, H315, H336, H361f, H373, H411
NaOH	H290, H314, H318
KMnO ₄	H272, H302, H314, H318, H361d, H373, H400, H410
nitromethane	H226, H302, H332, H351, H361d



P7. Breakfast of carbonyls

In this task we will continue differentiation of carbonyl compounds from each other and other chemicals as well.

You have seven compounds **1-7** marked as **A-G**. Alkⁿ is unknown alkyl chain, while substituent Rⁿ does not interfere with any reaction.





Equipment:

Item	Quantity
Nitrile gloves (S, M, L)	1
Paper tissues	1 pack
Vial (8 ml)	1
Measuring cylinder (10 ml)	1
Pasteur pipettes	16
Small spatula	1
Vials (2 ml)	14
Permanent marker	1
Glass capillaries/pipette tips	7
TLC plate with fluorescent indicator	1
Forceps	1
TLC chamber	1
Pencil	1
Ruler	1
254 nm UV lamp	1 (for the group of students)
Micropipette (100 μ L)	1
Tips for micropipette (100 μ L)	20
plate for UV-vis reader	1



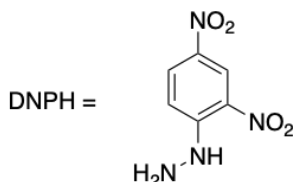
Chemicals:

Name	State	Concentration	Quantity (per student)	Placed in	Label
DNPH	Solid	-	0.05 g	Common reagent bottle	DNPH
H ₂ SO ₄	Solution (it must be freshly prepared)	1 ml of concentrated H ₂ SO ₄ in 10 ml of EtO	3 ml	Common reagent bottle	H ₂ SO ₄ in EtOH
Compounds 1-7	Solid/liquid	pure	0.2 g	vials	1,2,3,4,5,6,7
EtOH	liquid	-	5 ml	vial	EtOH
EtOAc	liquid	-	5 ml	vial	EtOAc
EtOAc:Hex = 1:7	solution	Mixture of EtOAc (1 ml) and hexane (7 ml)	8 ml	vial	EtOAc:Hex = 1:7
H ₂ O	liquid	-	20 ml	Common reagent bottle	H ₂ O
Tollens reagent	solution	-	3 ml	vial	Tollens
DNPH with unknown concentration	solution	-	1 ml	vial	DNPH unknown



Experimental procedure

Part A: Preparation of DNPH reagent



1. **Place** DNPH (0.05 g) in a 8 ml vial. **Mark** the vial as DNPH.
2. **Add** H₂SO₄ solution in EtOH (3 ml) to the vial with DNPH.
3. **Stir** the vial until all the solid is dissolved.

Part B: Analysis of unknowns

1. In case of liquid **place** two drops of an unknown compound in a vial. In case of solids, **place** place twice a tip-full of a small spatula of unknown and **add** ten drops of ethanol, **shake** cautiously until dissolved.
2. **Add** 20 drops of DNPH reagent prepared earlier to each unknown.
3. **Wait** for 10 mins
4. **Q1: Note** the observations in the table below.

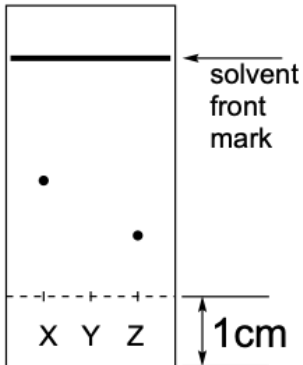
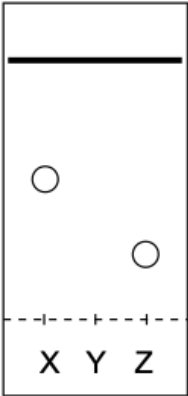
Sample	A	B	C	D	E	F	G
Observation							
P – precipitate							
N – no precipitate							

5. **Perform** the TLC analysis of the unknown samples. For this add one drop or one small spatula to the clean vial, add 1 ml of EtOAc to the vial. **Add** EtOAc (0.5 ml)



to the vial and **shake** cautiously.

6. **Prepare** the TLC plate(s). **Label** the starting line and **label** each spot with a letter corresponding to an unknown chemical.
7. **Load** the plate with chemicals using a glass capillary/pipette tip. **Put** one spot of 2-3 mm in diameter of each chemical to the corresponding place on the prepared TLC plate.
8. **Run** the TLC plate using EtOAc:Hex = 1:7 eluent.
9. **Remove** the plate from the TLC chamber. Mark the end of the front line.
10. **Use** 254 nm UV lamp to visualize the plate. Circle all the appeared spots.
11. **Q2: Sketch** the TLC plate according to the example shown below.

<i>a, example of the visualized TLC plate</i> 	<i>b, example of the TLC sketch according to the TLC example a</i> 	<i>c, place for the TLC sketch</i> 
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12. **Q3: Note** the observations in the table below.

Sample	A	B	C	D	E	F	G
Observation							
V – visible							
N – not visible							



13. **Heat** water until boiling.
14. **Perform** a Tollens test in a set of separate vials. For this **place** two drops/two small spatulas of each compound **A-G** in a vial.
15. **Add** 10 drops of Tollens reagent in each vial.
16. **Close** the cap, but not tightly.
17. **Place** boiling water in a beaker that can fit all vials (you need to have approximately 5-7 mm water layer so the vials will not float).
18. **Place** the vials in the water bath using forceps. **Wait** for 30-60 seconds. *Note: do not overheat the reaction mixtures and do not perform the reactions in boiling water. If so, repeat unsuccessful reactions again.*
19. **Q4: Write** the observations in the table below. *Note: A clear reaction should be observed. Repeat the experiment for the vials where the result is not clear enough.*

Sample	A	B	C	D	E	F	G
Observation P – positive Tollens test N – negative Tollens test							

20. **Q5: Assign** the structure of unknown chemicals below with structures **1-7**. If some chemicals cannot be differentiated after the tests performed, write down all the possible numbers that can be assigned to chemicals.

Sample	A	B	C	D	E	F	G
Unknown							

21. **Q6:** From the list below **choose** appropriate reagent(s) that can be used to figure out the remaining chemicals if any.

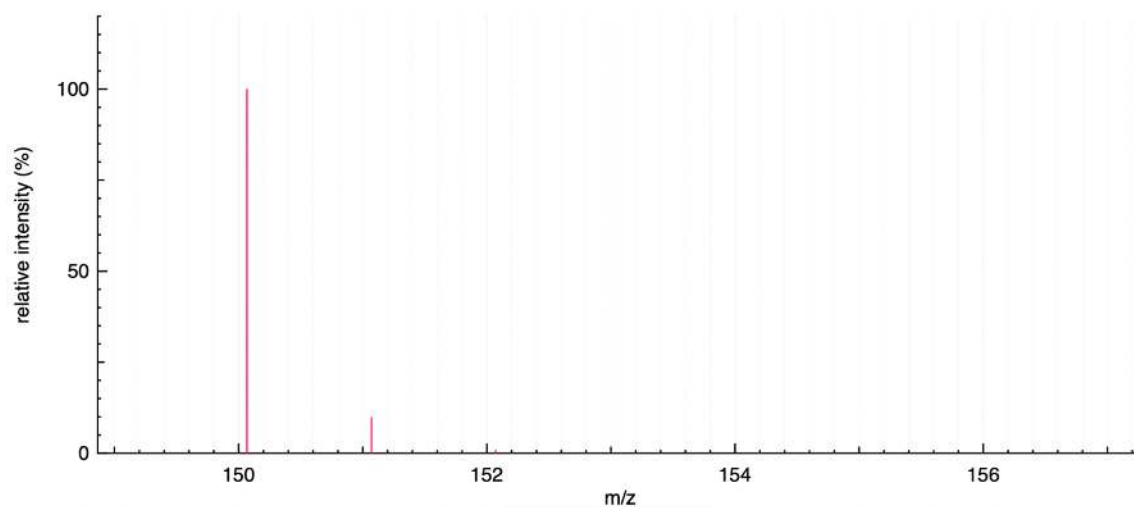
a) NaOH



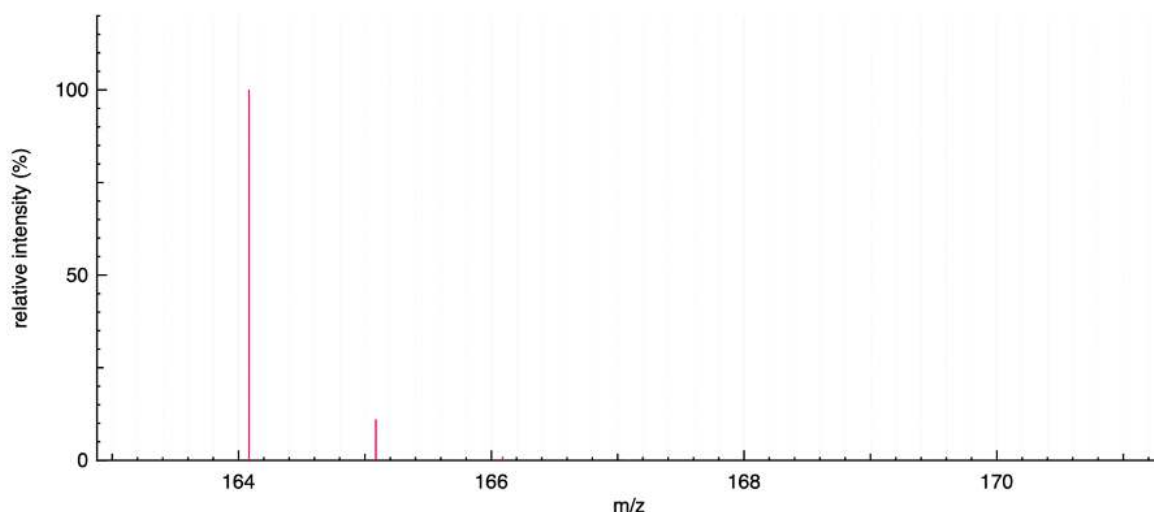
- b) NaOH , I_2
- c) EtOH
- d) $\text{Na}_2\text{S}_2\text{O}_3$, EtOH
- e) $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$, EtOH
- f) NaBH_4 , EtOH

22. **Q7: Analyse** the mass-spectra of the compounds **5** and **7** below and suggest their possible structures. Mass-spectra were recorded in positive mode with electron impact ionization method.

MS of 5



MS of 7



23. **Q8: Write** down a chemical transformation between two pairs if possible: **5** and DNPH reagent; **7** and DNPH reagent. If reaction is not possible, write so.

Part C: Analysis of DNPH concentration

You have a sample of DNPH with unknown concentration. The task is to identify the approximate concentration of DNPH in the solution by UV-vis spectroscopy with “eye-detector”.

1. **Prepare** a set of DNPH solutions. For this, use the UV-vis plate as a stand. **Place** 100 μL of DNPH solution (that was prepared in the part A) in the first slot of the UV-vis plate using micropipette.
2. **Take** 25 μL from the first slot and **add** it to the second slot. **Add** 75 μL of EtOH to the second slot (with a fresh pipette tip).
3. Gently **stir** the plate. **Replace** the pipette tip.
4. **Take** a sample of 25 μL from the second slot and return it to the second slot. **Repeat** this process for three times (this will help to mix the solution).
5. **Take** a sample of 25 μL from the second slot and **place** it in the third slot.
6. **Repeat** steps 6-8 until the final solution becomes completely colourless (or until 10 samples are prepared).
7. **Place** 75 μL of unknown DNPH sample in the second row of the plate.



8. **Place** the plate on a piece of white paper.
9. **Q9: Compare** the concentration of the unknown DNPH sample with the concentration of the prepared DNPH solution, e.g.:

$$5 \times c(\text{prepared}) < c(\text{unknown}) < 7 \times c(\text{prepared}).$$



GHS codes

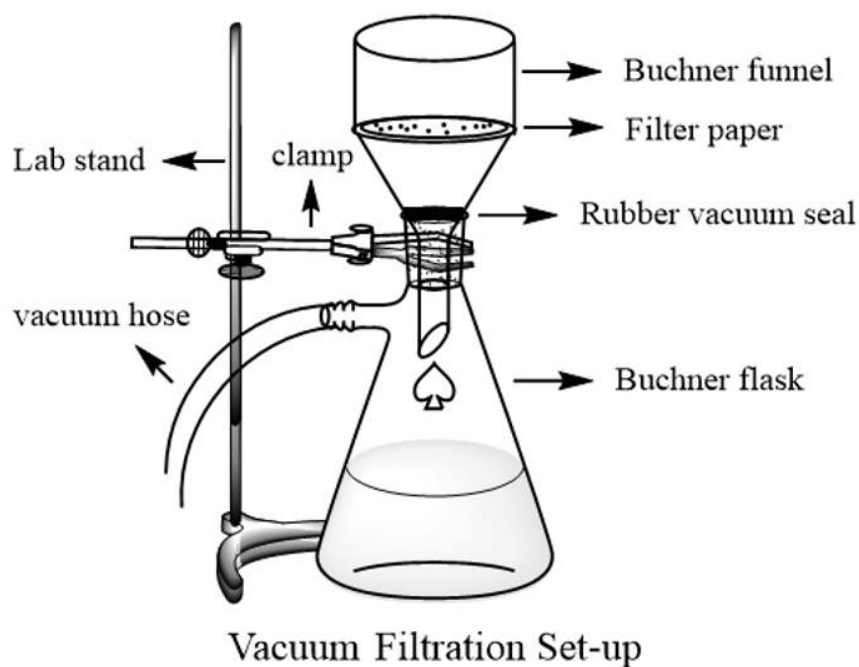
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Chemical	GHG code(s)
DNPH	H206, H302
H ₂ SO ₄	H290, H314
EtOH	H225, H319
EtOAc	H225, H319, H319
Hexane	H225, H304, H315, H336, H361f, H373, H411
H ₂ O	Highly toxic:)
Tollens reagent	H290, H302, H315, H319
1	
2	
3	
4	
5	
6	
7	



Standard procedure 1 - Vacuum filtration

Filtration is a physical process to separate the solid from the liquid by passing the mixture through a filter. Vacuum filtration uses suction to pull the solution or the mixture through the filter. The vacuum filtration apparatus consists of a Buchner flask (filter flask), Buchner funnel, filter paper, rubber vacuum seal (rubber adaptor), vacuum hose, and a vacuum pump. It is always recommended to mount the Buchner flask firmly to a lab stand using a three-fingered clamp.



General instructions for vacuum filtration

Safety note: It is recommended to cover the filter flask with a protective cover (e.g., piece of cloth); this will reduce the hazard in case the flask breaks under vacuum.

1. Mount the Buchner flask firmly to a lab stand using a three-fingered clamp.
2. Connect one end of the vacuum hose to the Buchner flask through the suction inlet and the other end to the vacuum valve on your bench.
3. Place the rubber vacuum seal on the top of the Buchner flask and place the Buchner funnel through the rubber seal.
4. Place the filter paper inside the Buchner funnel ensuring that the smooth side faces up (a gentle rub on both faces with your bare fingers will help you to



identify this).

5. Ensure that the filter paper sits flat inside the funnel and covers all the holes in the base of the funnel.
6. Moisten the filter paper with a few mL of distilled water (other solvents can be used depending on the experiment) and turn the vacuum on.
7. Inspect the suction by gently placing the palm of your hand on the top of the funnel.
8. Once you get a good suction, using a glass rod, deliver only small portions of the suspension to the filter paper and wait until the liquid has passed through before adding more so the that solid does not go to the edge of the funnel.
9. Once the solution is fully transferred, rinse the container with 2 mL of distilled water and pour through the filter paper.
10. Rinse the glass rod with a few mL of distilled water into the filter paper.
11. Once the liquid portions have gone through, close the vacuum, and wash the solid on the filter paper with a few mL of ice-cold distilled water.
12. Turn on the vacuum and allow the liquid to drain.
13. Repeat the washing process two times.
14. Let the air pass through the product for 5 min to dry it.
15. Close the vacuum and remove the hose from the flask by carefully applying pressure on the hose until the internal pressure in the flask equilibrates with the external pressure.
16. Using a spatula, gently take the filter paper out of the Buchner flask and scrape out the dried solid into a desired container and follow the experiment instructions. Only scrape gently to ensure bits of filter paper are not transferred.

Additional information

There are alternative filtration set-ups that can be used. For instance, the Buchner funnel can be replaced with a sintered funnel, which has a sintered disc embedded inside the glass funnel (see the pictures below). The disc can have different pore sizes and that allows us to perform the filtration without filter paper. These are used as the porosity of the disc is finer than that of the paper used with a Buchner funnel.



Filtration set-up with Buchner funnel



Filtration set-up with sintered funnel





Standard procedure 2 - Thin layer chromatography

There are different types of thin layer chromatography (TLC). Mostly, it is used to analyse chemicals (part A) and reaction mixtures (part B). Additionally, TLC plates can be visualised differently depending on the TLC plate used (part C). In this short manual we will consider most of the regular techniques as well as some basics of the results analysis (part D).

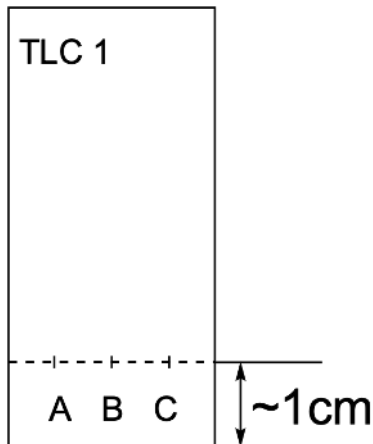
Part A: TLC analysis of chemicals

Let's say you have three unknown samples **A-C**. Each sample contains a certain chemical (they could be the same or different). Below we present a standard procedure for TLC analysis of chemicals **A-C**.

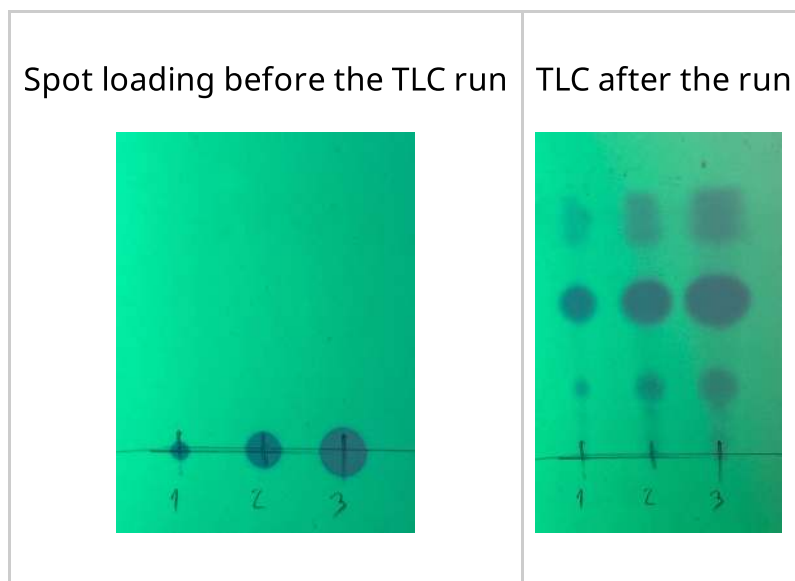
1. Prepare a TLC plate as shown in the figure below. Use the following instructions.
2. Be careful with the plate. If you touch it with your hand or a dirty glove, it can lead to some undesired spots. This can corrupt the interpretation of the TLC analysis.
3. You should use only pencil to label the plate (pen or marker can dissolve in the eluent and affect the separation).
4. Mark the starting line approximately 1 cm away from the bottom of the plate.
5. Mark three spots according to the chemical's abbreviation (**A-C**) at equal distance (~0.7-1 cm) apart and at least 0.5-1 cm away from the side of the plate.
6. Label the TLC plate with a pencil at the top according to the instructions in the task (we will label it as TLC 1).



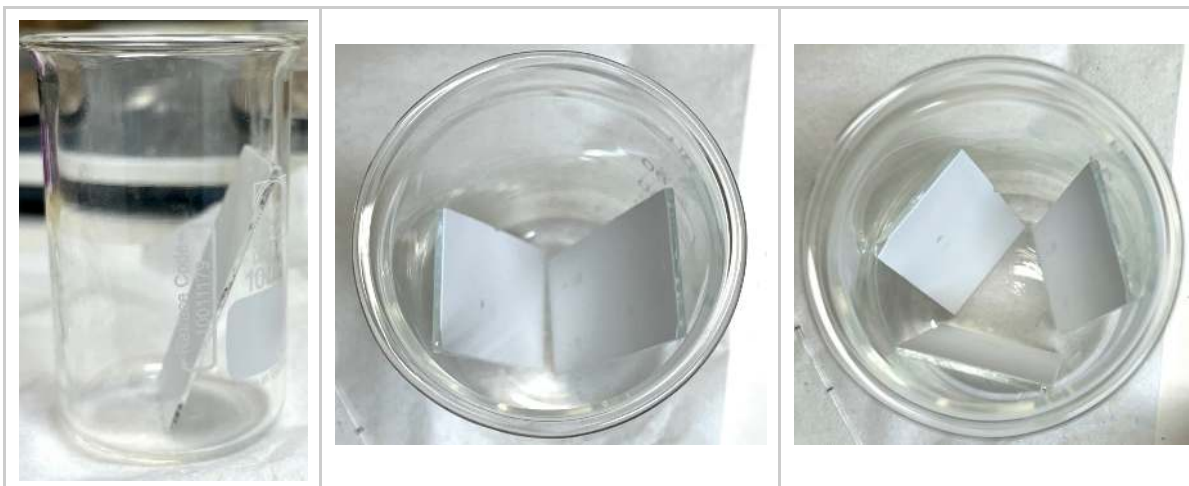
Example of TLC plate prepared for analysis of chemicals



7. Prepare a TLC chamber with the appropriate eluent using a pipette (we will use the mixture EtOAc:Hex = 1:6). If you accidentally pour too much eluent, you can discard it into a waste bottle (as we use organic solvents, we can discard the excess to the “organic waste”). Ensure that there is a piece of filter paper in the TLC chamber (it will increase the speed of the TLC run).
8. Label the TLC chamber with the eluent used using a marker (we will label the chamber as “1/6” which corresponds to the eluent).
9. Load the TLC plate with chemicals **A-C** using a glass capillary or pipette tip. Do not overload the plates, it is sufficient to load one tip of 1-2 mm in diameter for good visualisation; overloaded plates may lead to uninterpretable results. Compare three different spots for one chemical below under UV visualisation. Samples 1 and 2 are loaded nicely, while sample 3 is purposefully overloaded. The overloading in Sample 3 can affect the TLC in several ways. Firstly, there can be an overlap due to the big diameter of the spots. Also, it can affect an adjacent lane and change the retention factor of the spots there (there is only a small gap between the big spot in lane 3 and the same spot in lane 2, compare this with the gap between spots 1 and 2).



10. If you use a solution in organic solvent, ensure that the solvent evaporates completely after you have loaded the sample. The solvent residues can affect retention factor (especially if a rather non-polar eluent is used and the solution is prepared in polar solvent).
11. Use tweezers to place the TLC plate vertically in the chamber and run the plate (see the left picture below). You may place more than one TLC plate in the chamber if the size allows it (see the middle and right pictures below). If you put more than one TLC plate in, ensure that the solid phases of plates do not touch each other.



12. Close the chamber with a lid (for this, you may use a Petri dish or a watch glass; see the picture below). This will increase the speed of the TLC run.



13. Once the plate has run sufficiently, remove it from the chamber, mark the solvent front with a pencil immediately, before the solvent evaporates. We recommend running at least 6 cm of the plate for a good spot separation.
14. Dry the plate in the air until all visible solvent has evaporated.
15. Visualise the plate according to the task instructions (see part C).
16. **Do not forget to circle** all the visible spots right after visualisation.

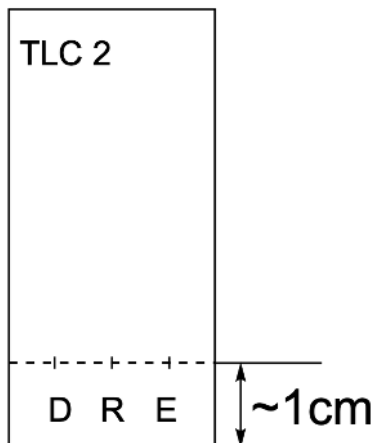
Part B: TLC analysis of a reaction mixture

Let's say you have two compounds **D** and **E** that can theoretically react with each other. A reaction has been performed and you have three samples: compounds **D** and **E** as well as reaction mixture **R**. Below we describe how to perform the TLC analysis of the reaction mixture.

1. Take a sample from the reaction mixture **R** and treat it according to the instructions in the task to get solution of **R**.
2. Prepare a TLC plate as shown in the figure below. Use the following instructions.
3. Mark the starting line approximately 1 cm away from the bottom of the plate.
4. Mark three spots: "D" for compound **D**, "R" for reaction mixture, and "E" for compound **E**. Mark them at equal distance (~0.7-1 cm) apart and at least 0.5-1 cm away from the side of the plate. It is recommended to put the reaction mixture spot R in the middle for better comparison with the starting materials.
5. Label the TLC plate with a pencil at the top according to the instructions in the task (we will label it as TLC 2).



Example of TLC plate prepared for analysis of the reaction mixture



6. Prepare a TLC chamber with the appropriate eluent using a pipette (we will use mixture EtOAc:Hex = 1:6). If you accidentally pour too much eluent, you can discard it into the waste bottle (as we use organic solvents, we can discard the excess to the “organic waste”). Ensure that there is a piece of filter paper in the TLC chamber (it will increase the speed of the TLC run).
7. Label the TLC chamber with the eluent used using a marker (we will label the chamber as “1/6” which corresponds to the eluent).
8. Load the TLC plate with chemicals **D** and **E** as well as reaction mixture **R**. Use a glass capillary or pipette tip. Do not overload the plates, it is sufficient to load one tip of 1-2 mm in diameter for good visualisation; overloaded plates may lead to uninterpretable results.
9. If you use a solution in organic solvent, ensure that the solvent evaporates completely after you have loaded the sample. The solvent residues can affect retention factor (especially if a rather non-polar eluent is used and the solution is prepared in polar solvent).
10. Use tweezers to place the TLC plate vertically in the chamber and run the plate.
11. Once the plate has run sufficiently, remove it from the chamber, mark the solvent front with a pencil. We recommend running at least 6 cm of the plate for a good spot separation.
12. Dry the plates in the air until all visible solvent has evaporated.
13. Visualise the plate according to the task instructions (see part C).
14. **Do not forget to circle** all the visible spots right after visualisation.

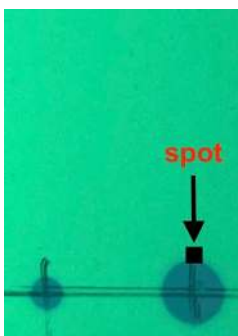


Part C: Visualisation of TLC plates

Let's say you have run the TLC and the compounds under investigation are colourless. To see the spots, one needs to visualise the plate using one of the following techniques:

UV light visualisation of the TLC plate. A specific type of TLC plate is required to use this method (except for the rare cases when the compound under investigation is itself fluorescent); the stationary phase should contain a fluorescent material. When UV light is shone on the plate, the background of the plate appears in green, while the spots are darker for the chemicals that absorb UV light (see the picture below).

Safety note: DO NOT look directly into the source of UV light, minimise the exposure of UV light to the eyes and skin.



Staining the TLC plate. If the TLC plate does not contain any fluorescent material or the compounds do not absorb UV light, a technique called "staining" can be applied to visualise the plate (see the picture below, phosphomolybdic acid stain was used to visualise this plate).



A staining reagent (or just stain) should react/interact in some way with the chemicals on the plate to change the colour. As a result, the spots become visible in comparison with the rest of the TLC plate. Not necessarily all the spots will react



with the stain reagent, some of them might remain invisible for one stain or another.

There are different stains that can be applied to visualise the compounds on the TLC plate. Sometimes the stain gives the results straight away, while in other cases it is necessary to heat the TLC plate to develop it (which should be stated in the guidelines). To heat a plate it is possible to use:

- a heat gun which blows hot air out of its nozzle,
- a hotplate that is covered with some protective surface (such as aluminium foil).

In both cases it is necessary to avoid touching the hot area with your fingers. We recommend to use tweezers to handle the TLC plates during the heating process.

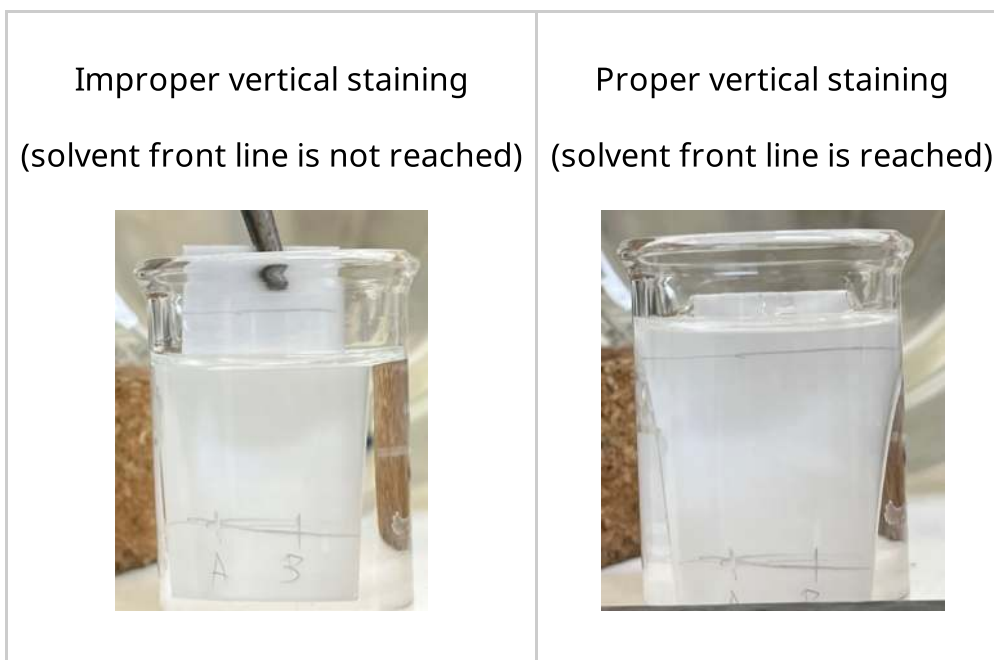
Regardless of the stain, there are three options of how to place the TLC plate in the stain chamber described below.

Vertical staining

The standard technique to use any stain is to dip the plate vertically in the staining liquid. The dipping and plate removal should be fast enough to prevent diffusion of the spots.

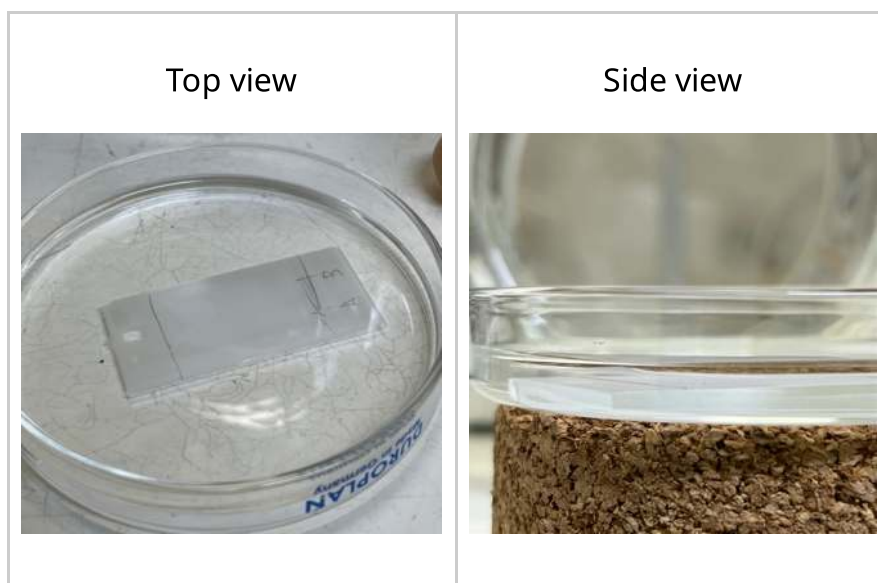


When performing any staining, ensure that the plate is covered in the staining reagent up to the solvent front line. Otherwise, some spots can be missed and not seen.



Horizontal staining

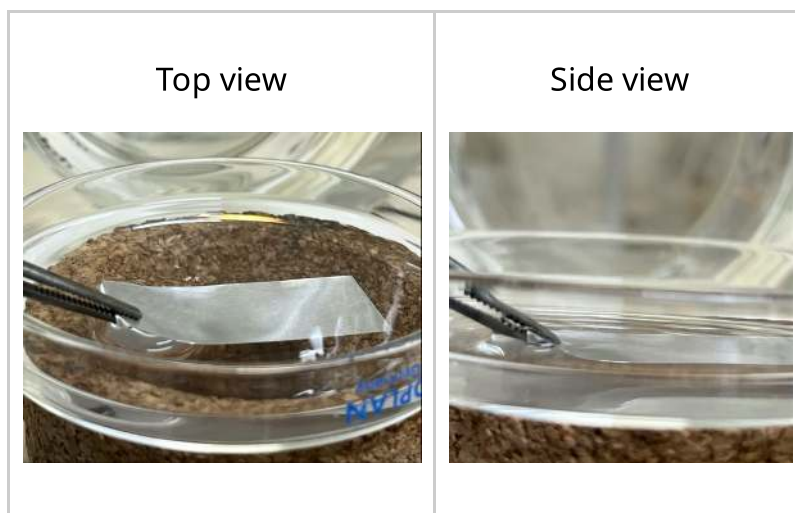
Horizontal staining is similar to vertical staining, however, the staining reagent is placed in a wide container (for instance, a Petri dish). This allows us to reduce the amount of stain used. The TLC plate can be placed facing up as shown below. However, in this case the plate can be unequally stained if not dipped completely.



The TLC plate can alternatively be placed facing down as shown below. This is the preferable way of horizontal staining for aluminium TLC plates, as they can be easily



bent as demonstrated in the pictures. However, the staining should be performed carefully because the plate can be unequally stained if not dipped completely.



Staining by spraying/pouring

This method allows us to use small quantities of the stain reagent as well. The TLC plate is placed in a container (for instance, a Petri dish) and a staining reagent is sprayed or poured over the plate. However, spraying can generate unnecessary smell and more extensive evaporation of the staining reagent. Therefore, necessary precautions should be taken in order to use this technique.

As can be seen from the pictures below, pouring of the stain often generates unnecessary fronts of the reagent which can corrupt the TLC picture. Therefore, spraying is a preferred option.

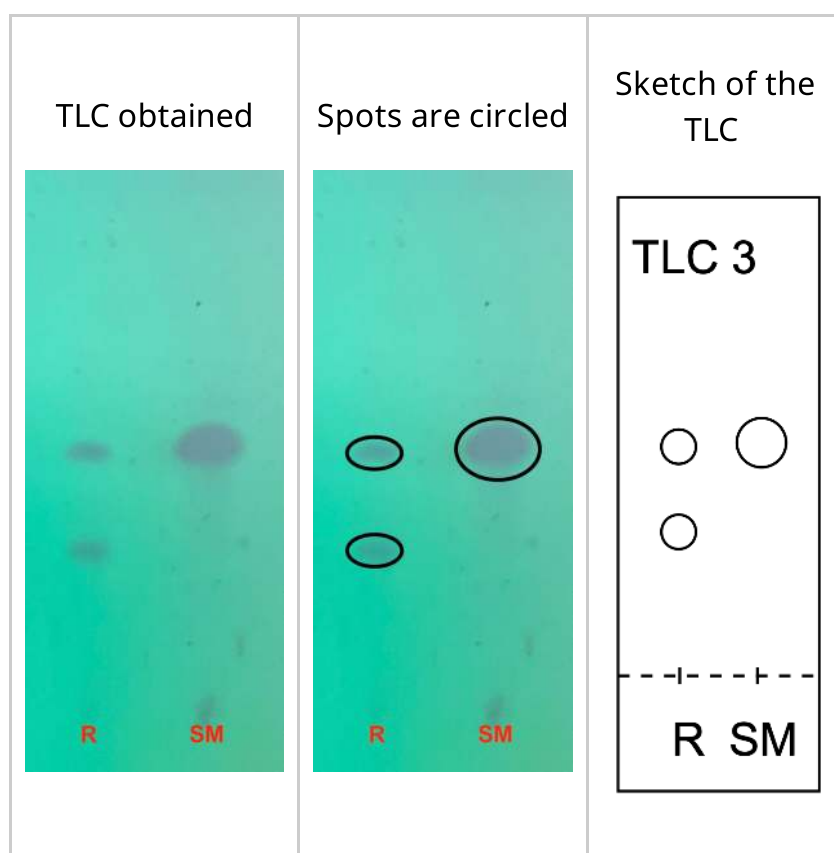




Part D: Analysis of the results

After the TLC has been developed, the results have to be analysed.

Let's say we performed a reaction from a certain starting material SM and obtained a reaction mixture R. According to all the instructions, we ran TLC analysis and visualised the plate with UV light. As such, we obtained a TLC picture (see the left picture below). Hopefully, you see the mistake that was done when the TLC was performed, don't you?



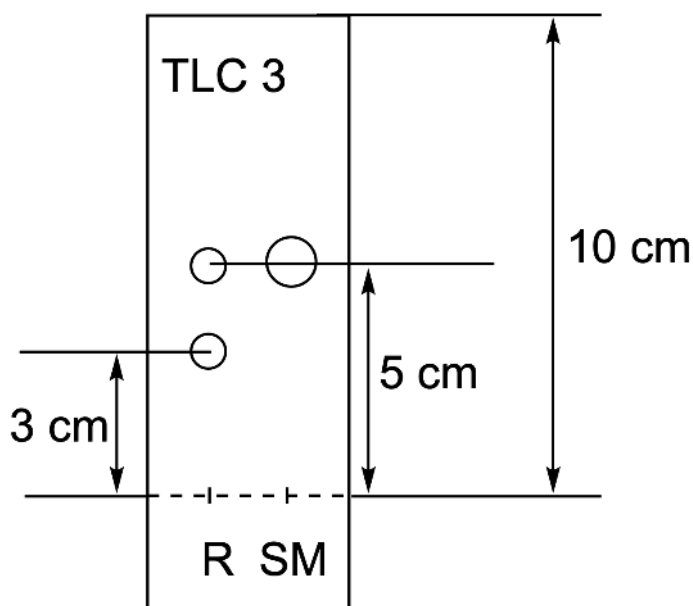
Unfortunately, the person who performed the TLC forgot to mark the starting line and the solvent front line. Luckily, we still can see the start because of some impurity in the SM (small spot at the bottom of the line "SM"). Let's assume that the TLC had been run until the end of the picture.

Standard analysis of the TLC usually includes the following steps:

1. **Circle** all the spots as shown in the middle picture above.
2. **Draw** a sketch of the TLC (similar to what is shown on the right) if you are required to do so by the task.



3. As one can see from the TLC, a new spot appeared below the one that corresponds to the SM. Potentially, this is the reaction product.
4. We notice that the spot of the SM has not disappeared yet. Therefore, we can assume that this reaction has started, but it also needs some additional time to be complete.
5. In some tasks you will be required to measure the **retention factor** (R_f) for the spots on the TLC plate. To do so, you need to perform the following steps. We will consider the only spot on the lane "SM". All the other spots should be treated similarly.
6. **Measure** the distance between the starting line and solvent front line (10 cm in the picture below). This is the distance that the solvent travelled.
7. **Measure** the distance between the starting line and the middle of a certain spot (e.g., 5 cm for the spot on the right lane "SM"). This is the distance that the compound travelled.



8. The retention factor for the spot SM can be calculated according to the equation below. This will give the relative R_f value which will be approximately the same for TLCs run with plates of different length, but with the same eluent and stationary phase.
$$R_f = (\text{distance travelled by the compound}) / (\text{distance travelled by the solvent})$$
9. For the spot on the right lane: $R_f = 5 / 10 = 0.5$.
10. In general, the R_f value depends on the stationary and mobile phases used.
11. If a compound prefers to interact with the stationary phase rather than with the mobile phase, its R_f value will be small (usually, $R_f < 0.5$). For most TLC



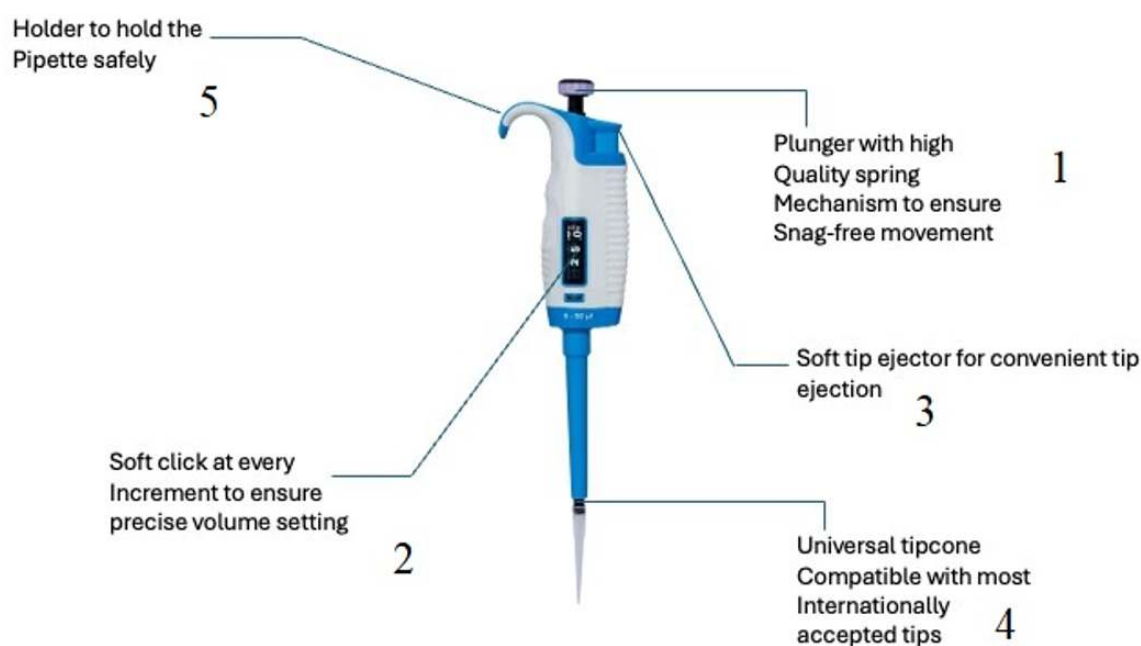
plates, a Si-gel stationary phase is used, which is quite polar. Therefore, the compounds that will stay at the bottom of the plate are the more polar compounds.

12. If a compound prefers to interact with the mobile phase rather than with the stationary phase, its R_f value will be big (usually, $R_f > 0.5$). Again, for a polar Si-gel stationary phase, the compounds that will go to the top of the plate the the more non-polar (or less polar) compounds.
13. In the example above, there are two spots on the left lane "R". The top one has $R_f = 0.5$, while the lower one has $R_f = 0.3$. From this information we can infer that the bottom spot (the product) is more polar than the top spot (the starting material).



Standard procedure 3 - Use of a micropipette

Micropipettes are used to measure and transfer small amounts of liquids (typically in the 1 μL to 1000 μL range). Note that there are different types of micropipettes for different volumes in this range. Any particular micropipette is typically only accurate over part of this range, e.g. 20 μL to 200 μL ; ensure to check the range before using.



General instructions for micropipette operation

1. Setting the delivery volume

- Set the delivery volume using the push button on the top of the micropipette (1). To increase the delivery volume, turn the push button counter-clockwise. To decrease the delivery volume, turn it clockwise.
- Note:* micropipettes from other manufacturers can have different designs of the ring used to adjust volume. If you have trouble in finding or using it, approach your lab assistant.
- Ensure that the desired delivery volume clicks into place. Check the volume reading at window 2.



- d. Do not set a volume that lies outside the micropipette's specified volume range. Using excessive force to turn the push button outside the range may jam the mechanism and eventually damage the micropipette.

2. Tip ejection

- a. In order to eject the tip, point the micropipette at a suitable waste container and press the ejector button (3) with your thumb.

3. Pipetting

- a. Press and release the push button (1) slowly. Do not allow it to snap.
- b. Ensure that the tip is firmly attached to the tip cone (4).
- c. Before you begin your actual work, fill and empty the tip 2-3 times with the reagent or solution that you will be pipetting.
- d. Hold the micropipette in an upright position while aspirating. The holder (5) must rest on your index finger.
- e. Fill a clean reagent/solution reservoir with the reagent/solution to be dispensed.
- f. Press the push button (1) till the first stop.
- g. Dip the tip under the upper surface of the reagent/solution in the reservoir, to a depth of about 1 cm.
- h. Slowly release the push button.
- i. Withdraw the tip from the reagent/solution.
- j. Touch the tip against the edge of the reservoir to remove any excess reagent/solution.
- k. Deliver the reagent/solution by gently pressing the push button till the first stop. After a delay of about one second, stop. This action will empty the tip.
- l. Release the push button to let it retract to the ready position. If necessary, change the tip and continue pipetting. Always use a new, clean tip when pipetting a new reagent/solution.



أولمبياد الكيمياء الدولي السابع والخمسون
الإمارات العربية المتحدة
57th ICHO - United Arab Emirates - 2025

ICHO 2025

Solutions

Theory Prep Problems

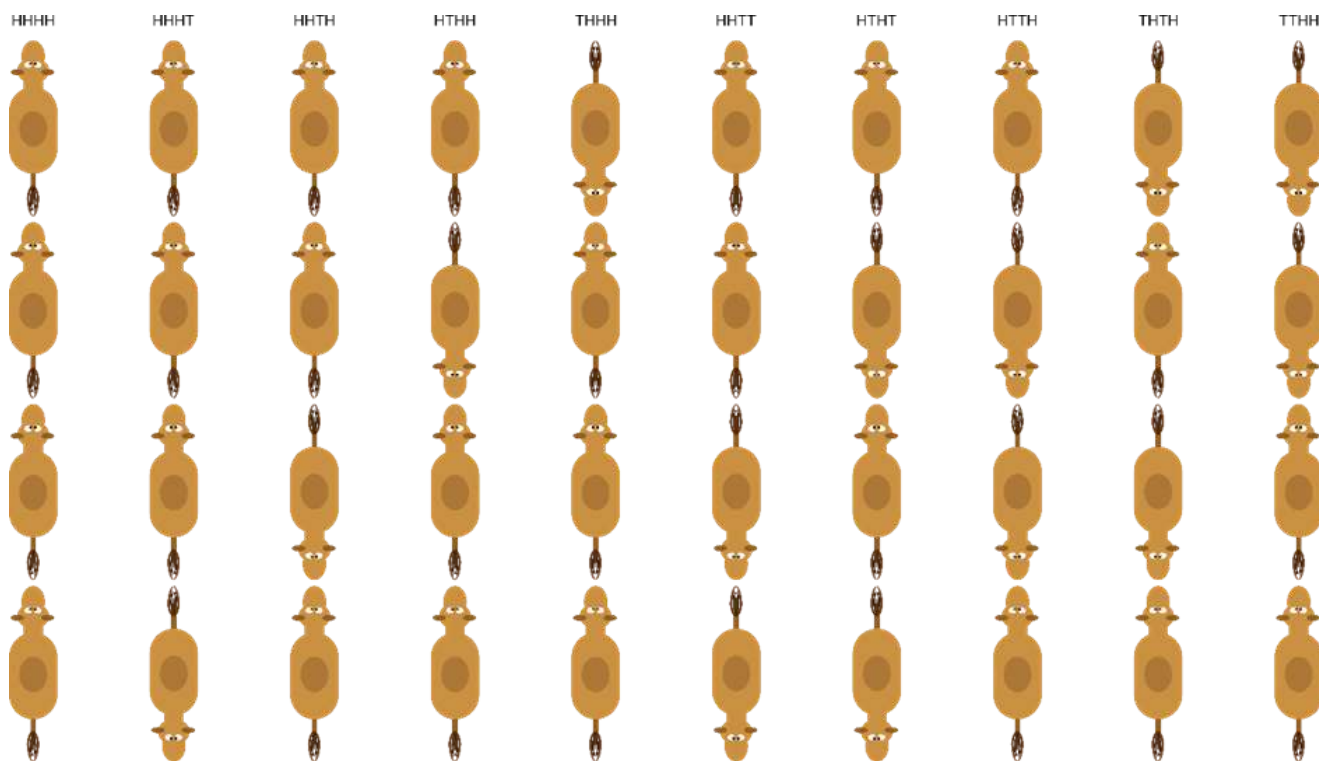


1. Stereocamelstry

(a) There are four possible arrangements: HHH, HHT, HTH, and THH.

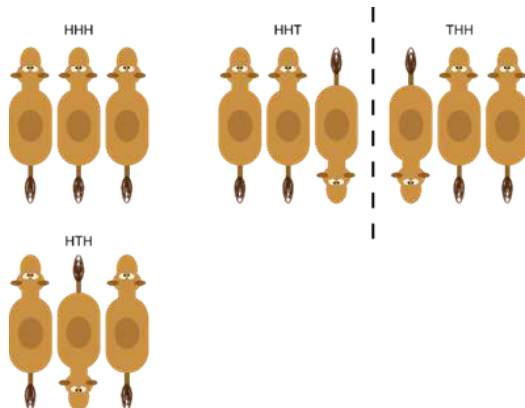


(b) There are ten possible arrangements: HHHH, HHHT, HHHT, HTHH, THHH, HHTT, HTHT, HTTH, THTH, TTHH.

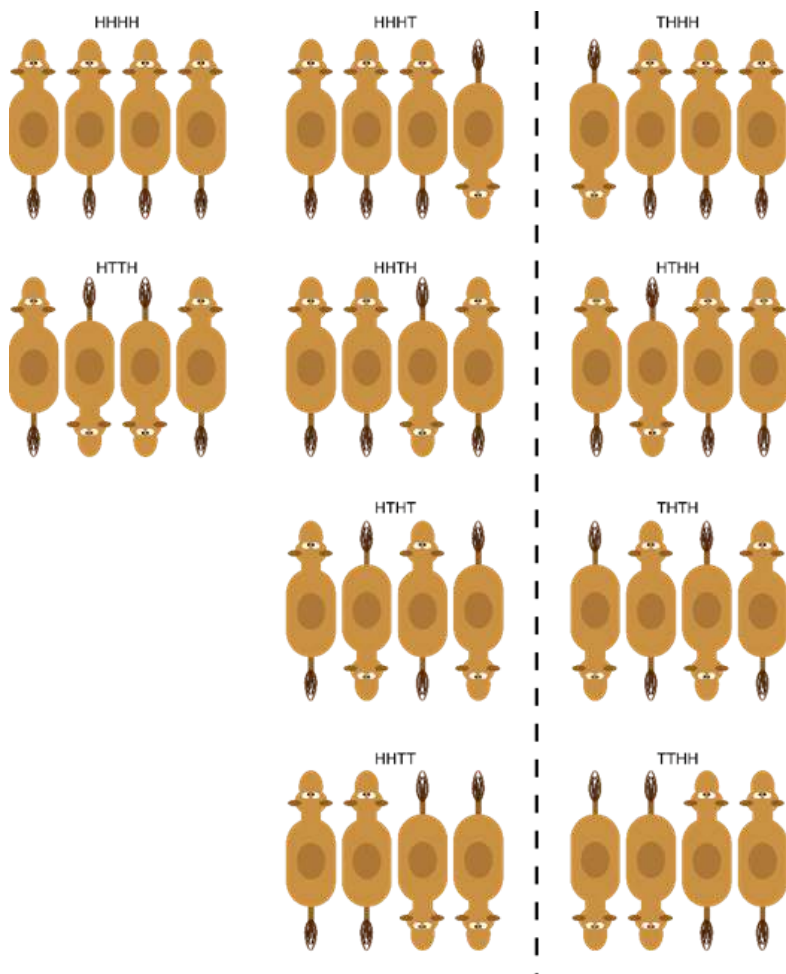




(c) There are four possible arrangements. The achiral arrangements are HHH and HTH. There is one pair of chiral arrangements (HHT and THH).

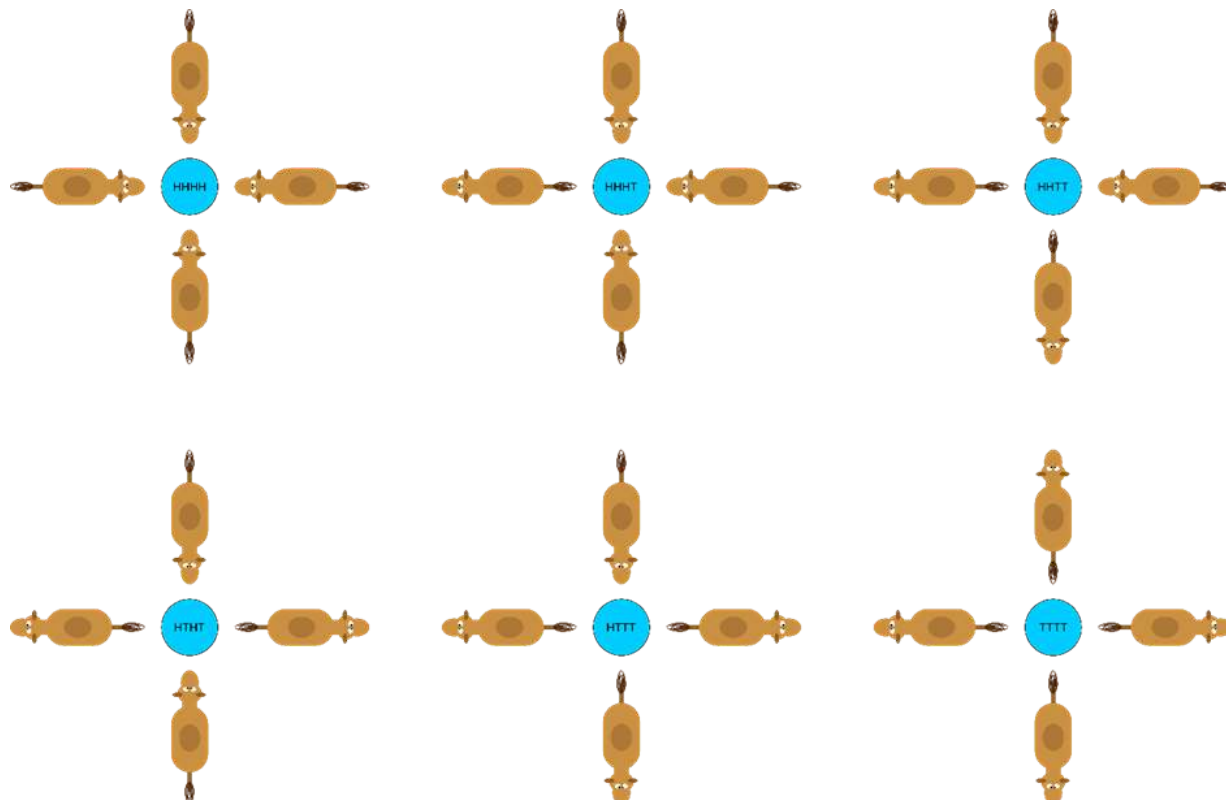


(d) There are ten possible arrangements. The achiral arrangements are HHHH and HTTH. There are four pairs of chiral arrangements (HHHT and THHH), (HHTH and HTHH), (HTHT and THTH), and (HHTT and TT HH).

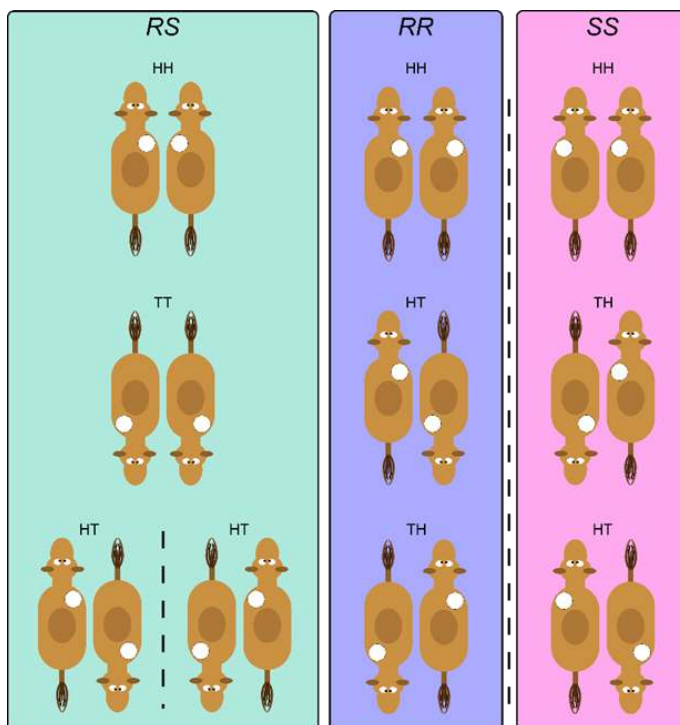




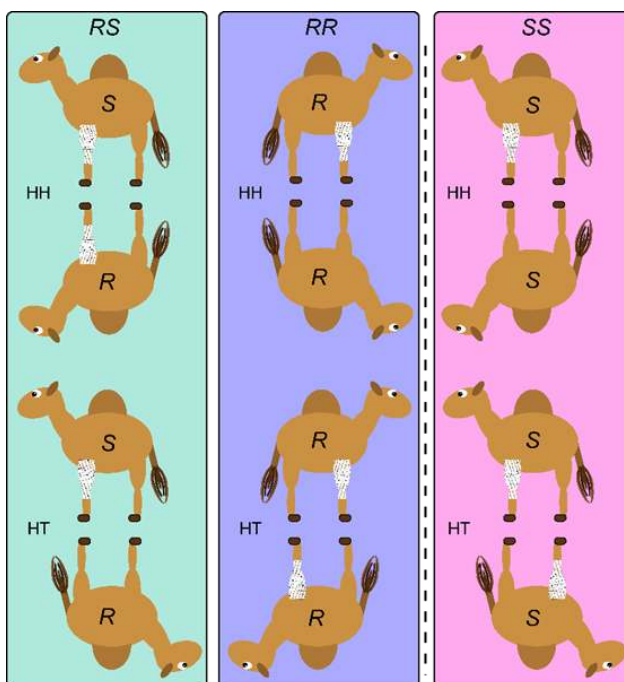
(e) There are six possible arrangements. All of them are achiral. Describing the arrangements clockwise from the 12 o'clock position, there is: HHHH, HHHT, HHTT, HTHT, HTTT, and TTTT.



(f) There are ten possible arrangements. There are three possible arrangements where the two camels are both *R* (HH, HT, and TH). All three of these arrangements are chiral and their enantiomeric arrangements are the three possible arrangements where the two camels are *S*. There are four possible arrangements where one camel is *R* and one camel is *S* (HH, TT, HT, and TH). Note that this is one more arrangement than when the camels were individually achiral. Here, the HH and TT arrangements are not the same as one arrangement has the injured legs on the inside and one has the injured legs on the outside. The HH and TT arrangements are overall achiral as they both have mirror plane symmetry down the middle. The HT arrangement is the enantiomer of the TH arrangement.

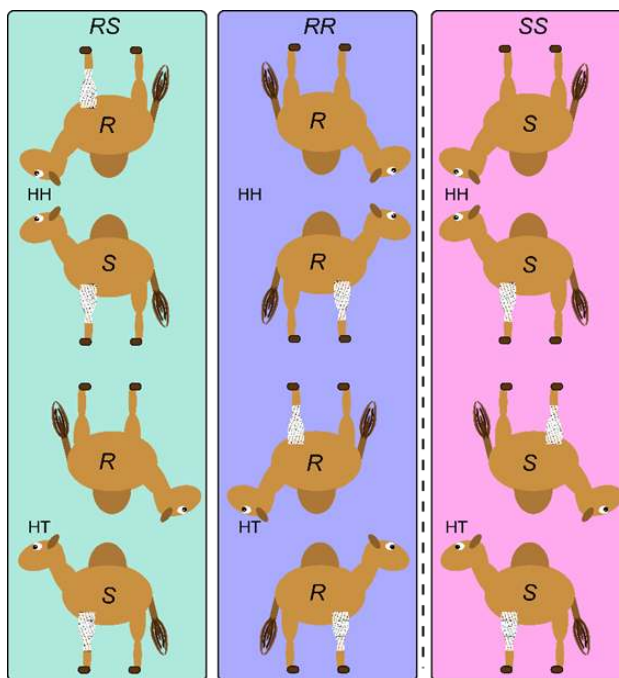


(g) There are six possible arrangements. There are two possible arrangements where the two camels are both *R* (HH and HT). Both arrangements are chiral, and their enantiomeric arrangements are the two possible arrangements where the two camels are *S*. There are two possible arrangements where one camel is *R*, and one camel is *S* (HH and HT). The HH and HT arrangements are both overall achiral. The HH arrangement has a mirror plane, and the HT arrangement has a centre of inversion.

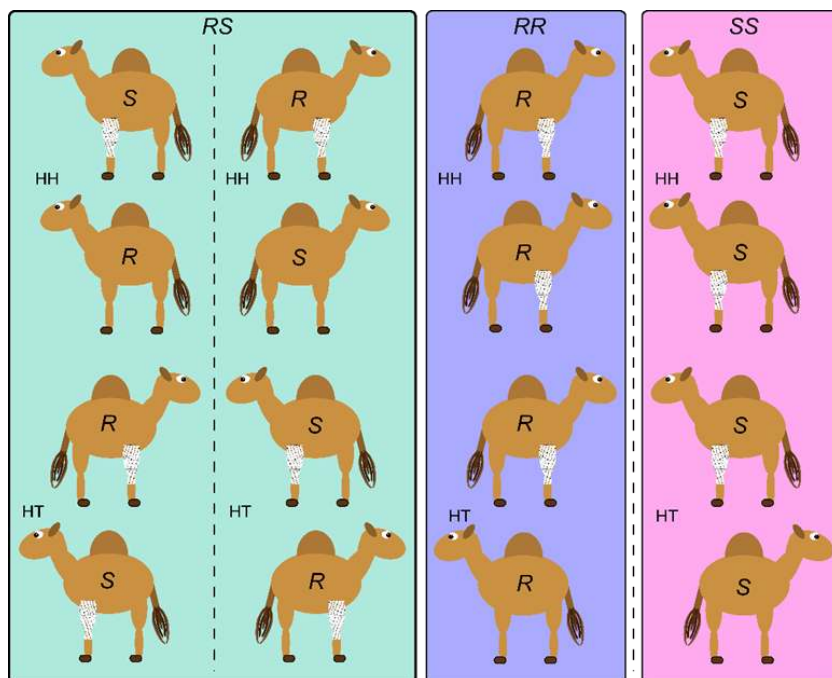




(h) This is an identical situation to the previous one. There are six possible arrangements. There are two possible arrangements where the two camels are both *R* (HH and HT). Both arrangements are chiral, and their enantiomeric arrangements are the two possible arrangements where the two camels are *S*. There are two possible arrangements where one camel is *R*, and one camel is *S* (HH and HT). The HH and HT arrangements are both overall achiral. The HH arrangement has a mirror plane, and the HT arrangement has a centre of inversion.

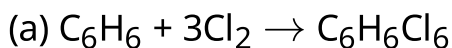


(i) There are eight possible arrangements. There are two possible arrangements where the two camels are both *R* (HH and HT). Both arrangements are chiral, and their enantiomeric arrangements are the two possible arrangements where the two camels are *S*. There are now four possible arrangements where one camel is *R*, and one camel is *S*. There is one pair of enantiomeric HH arrangements and one pair of enantiomeric HT arrangements. There is no longer any mirror plane or centre of inversion symmetry in these *RS* arrangements. They differ in which camel has its hump closest and which camel has its feet closest to the other camel.



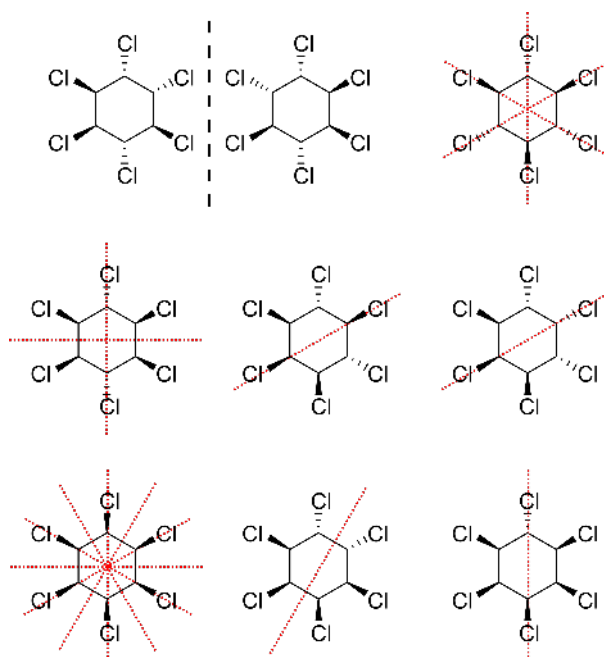


2. Mirror, mirror plane on the wall, who's the deadliest of them all?

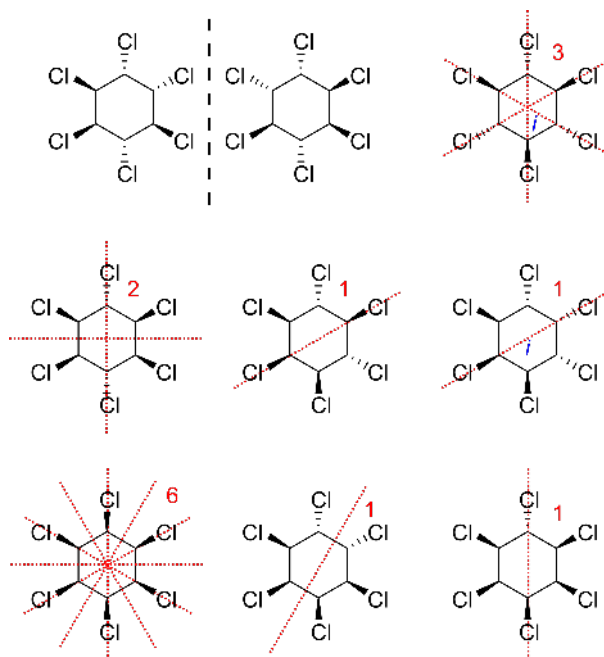


The reaction proceeds via a free-radical addition reaction rather than a substitution reaction due to the relatively high strength of the C–H bonds. Whilst Faraday noted the formation of muriatic acid (now called hydrochloric acid), if the addition reaction proceeds cleanly then HCl is not formed. The HCl may have been from impurities in Faraday's samples. Modern techniques show that Faraday's starting material for the isolation of benzene likely was a mixture of at least 300 compounds.

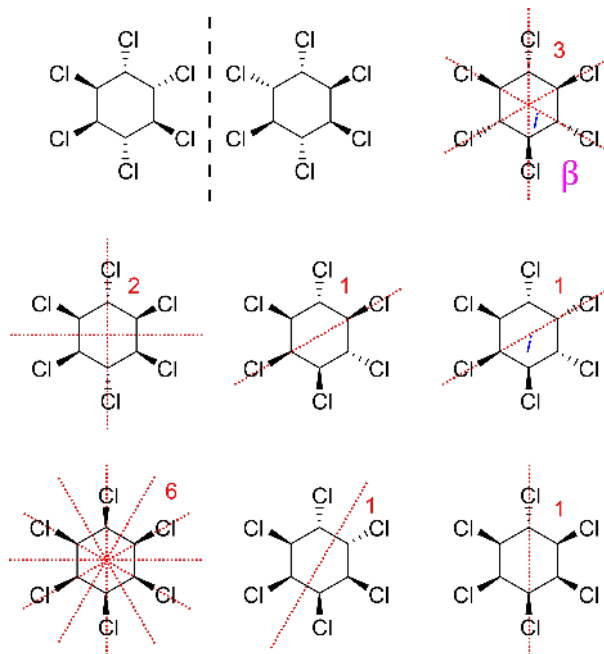
(b) There are nine stereoisomers of **HCH**. There is one pair of enantiomers and seven achiral structures. Mirror planes are identified with red lines.



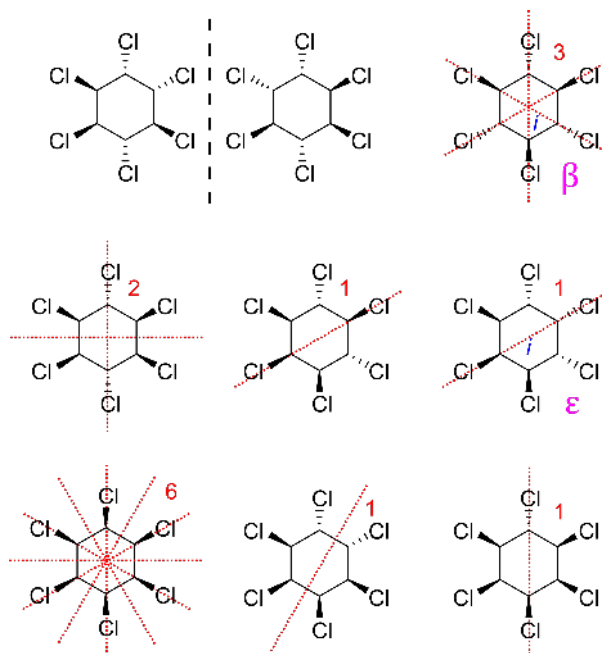
(c) First, we can count the number of planes of symmetry in each structure and label whether the structures have centre of inversion symmetry (*i*).



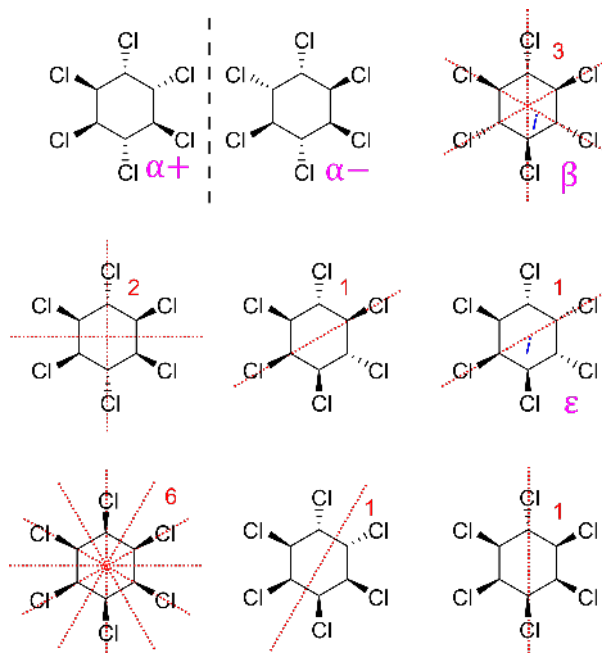
The most useful piece of information is the final clue: *The β isomer has by far the lowest chemical reactivity.* This is the isomer with the Cl atoms alternating on the top and bottom. See part **(d)** for explanation. This allows the β isomer to be assigned.



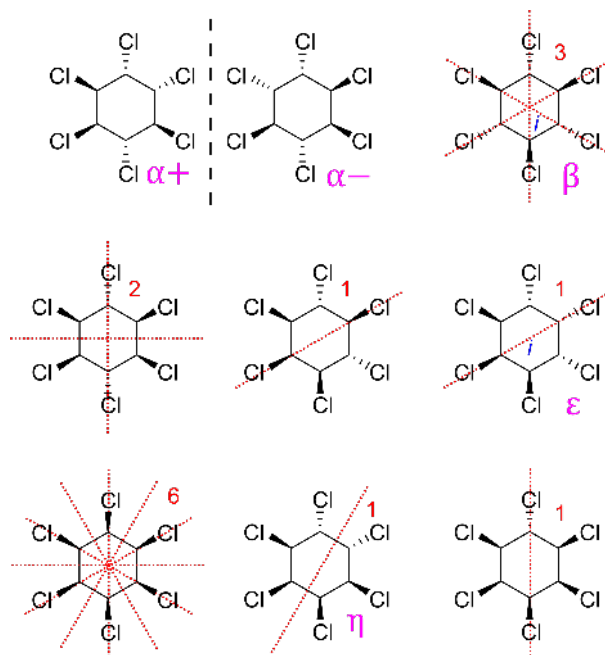
We can then use the first clue: *The β and ϵ isomers contain centres of inversion,* to identify the ϵ isomer.



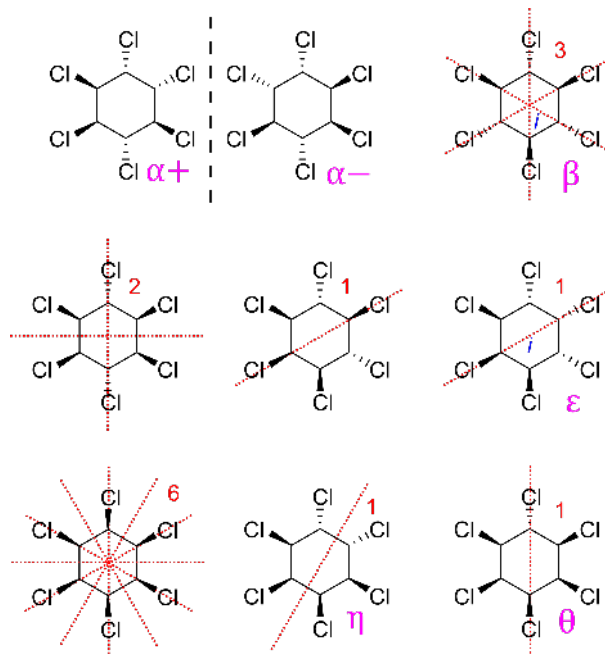
Only two of the nine isomers are chiral. Given we know from the sixth clue: *The + and - refer to dextrorotatory and levorotatory respectively*, it would make sense for the α^+ and α^- isomers to be the chiral ones. From the information given we cannot assign which is which, as $+/-$ cannot be determined from chemical structure drawings. They have been assigned here for information.



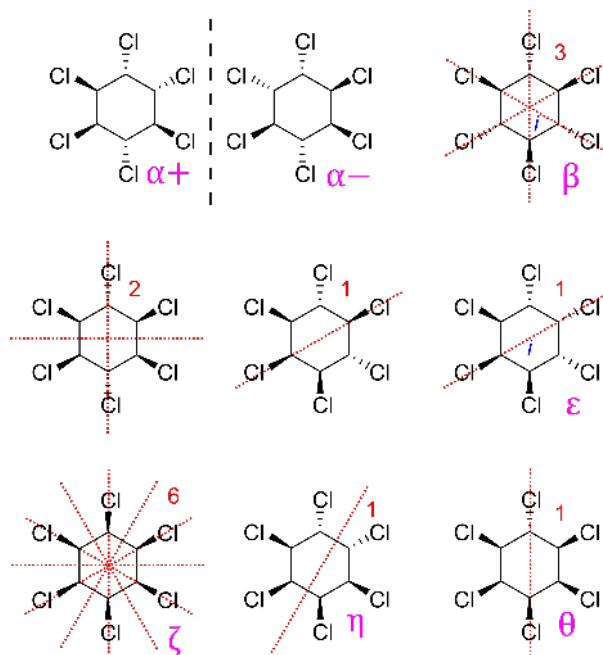
The fifth clue: *The η isomer does not possess a plane of symmetry through any of the atoms*, allows us to assign the η isomer, as this is the only one remaining with no plane of symmetry through any of the atoms.



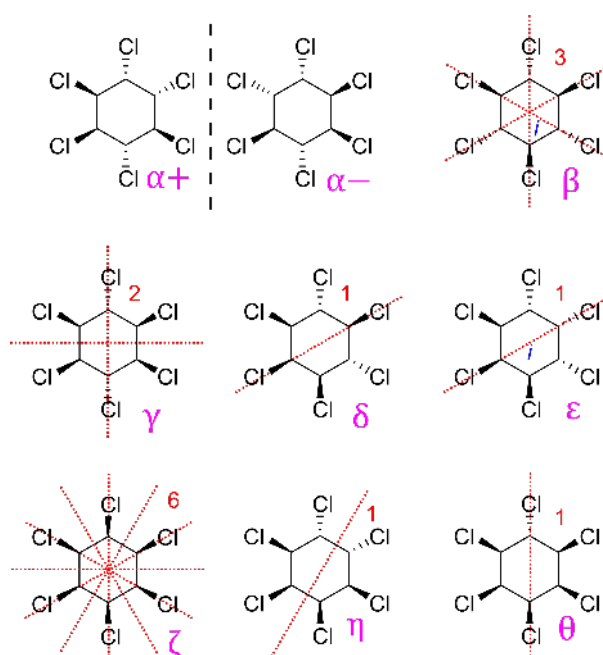
As epimers only differ in configuration at one centre, the third clue: *The θ isomer is an epimer of the η isomer*, now allows us to identify the θ isomer as there is only one compound that is an epimer of the η isomer remaining.



The second clue: *The ζ isomer is not an epimer of the α^+ isomer*, now allows us to identify the ζ isomer.



The fourth clue: *The γ isomer has more planes of symmetry than the δ isomer*, allows us to assign the γ isomer and the δ isomer to the remaining two structures.

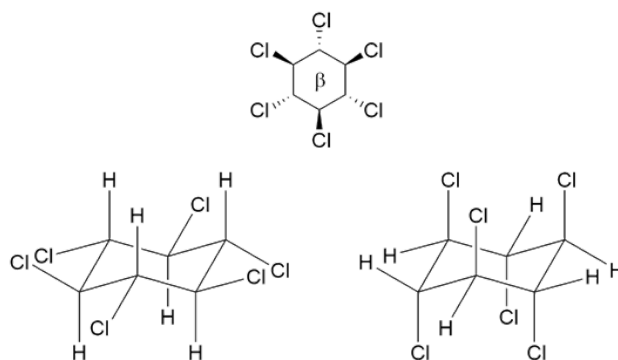


(d) The β isomer has the lowest chemical reactivity as this is the only isomer where all neighbouring Cl are *trans* to each other. Possible degradation pathways for **HCH** might include substitution or elimination. However, the presence of a Cl atom on each carbon sterically hinders the approach of nucleophiles, making substitution slow.

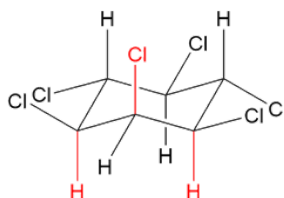


Elimination most readily proceeds via an antiperiplanar transition state. This requires a *trans* H and Cl (so both substituents must be in axial positions in a chair conformation). The β isomer is the only isomer which does not possess this in either possible chair conformation. The β isomer sits in the chair conformation with all Cl in equatorial positions (this is the only isomer where this is possible). The other chair conformation where all the Cl are axial is much higher in energy, however this is still not reactive as there is no *trans* H and Cl.

All the other isomers possess at least one *trans* H and Cl, which can sit antiperiplanar to each other in a chair conformation. Therefore, this makes the β isomer the least reactive.

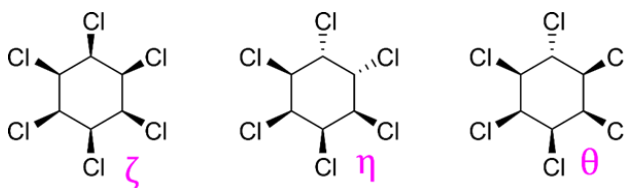


No antiperiplanar H and Cl in either chair conformation



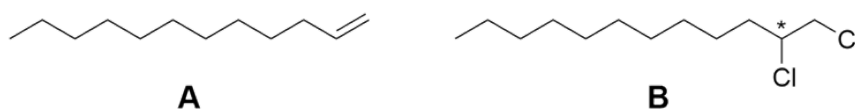
All other isomers can access one chair conformation which has at least one antiperiplanar H and Cl. This can eliminate HCl much more quickly.

(e) The ζ -**HCH**, η -**HCH**, and θ -**HCH** isomers all have at least four adjacent Cl atoms that are *cis* to each other (on the same face of the cyclohexane ring). Radical addition reactions are often not stereospecific, meaning all possible isomers can form. Cl is a much larger substituent than H, and so it becomes progressively less likely for additional Cl atoms to be added to the same face as existing Cl atoms over the course of the reaction due to steric hindrance, particularly on neighbouring atoms.

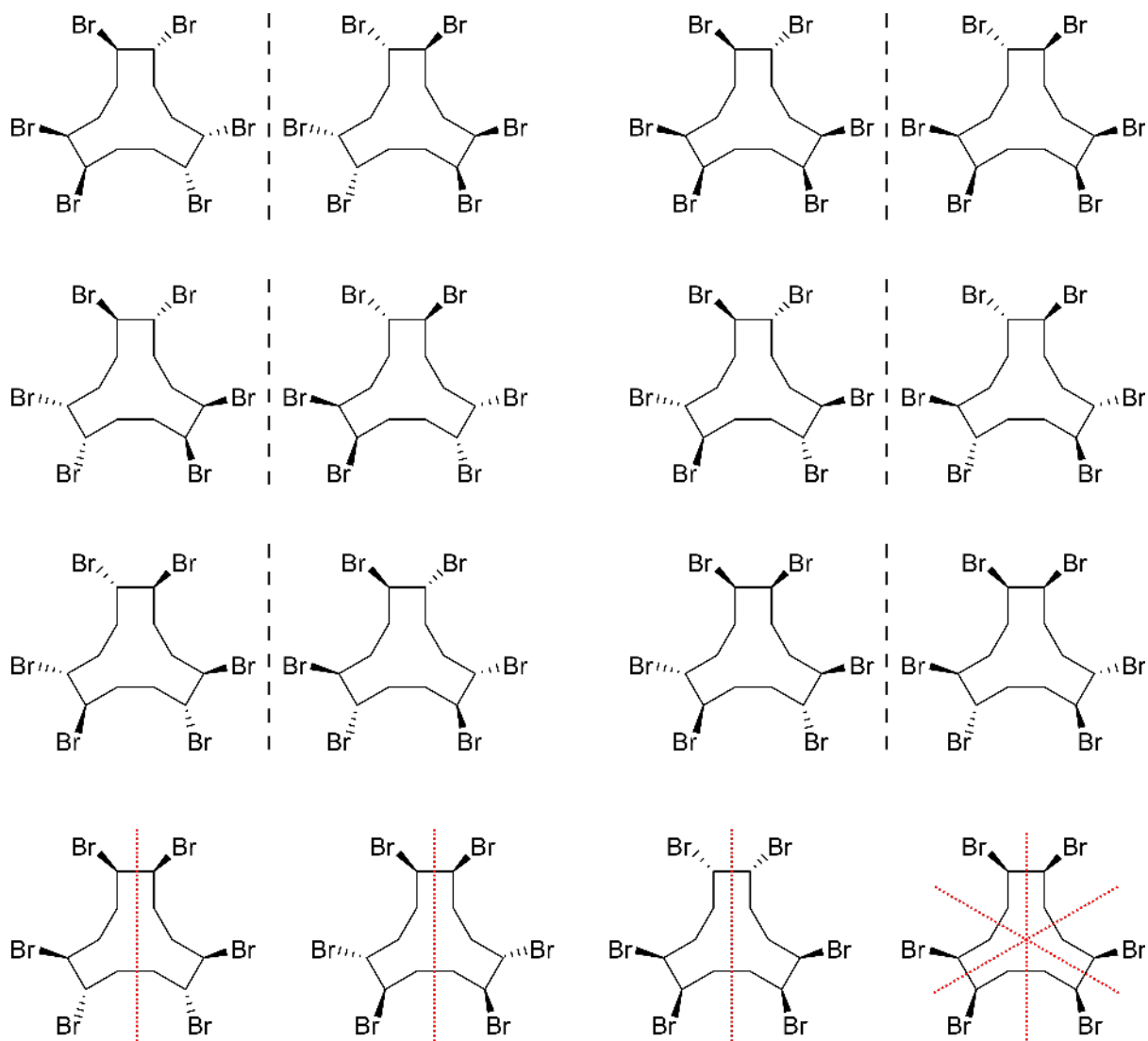


(f) The formula for **B** is $C_{12}H_{24}Cl_2$. The chlorine isotope pattern is the key indicator here. Cl is approximately 75% ^{35}Cl and 25% ^{37}Cl . We might first guess **B** contains two Cl atoms (formal addition of Cl_2 across one alkene). The relative intensity of the 240.122 peak compared to the 238.125 peak is consistent with this. Note the presence of ^{13}C complicates these isotope patterns. If product **B** contains two Cl, then its general formula must be $C_nH_{2n}Cl_2$. We can then work out that **B** is $C_{12}H_{24}Cl_2$.

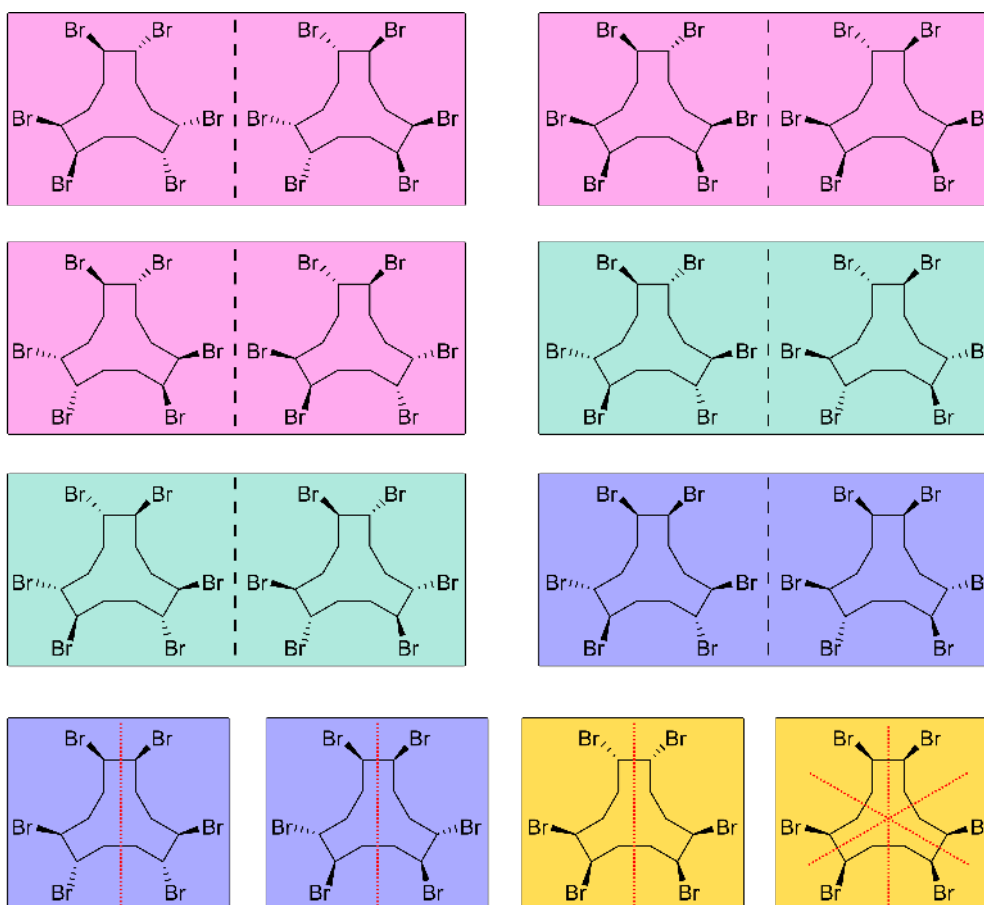
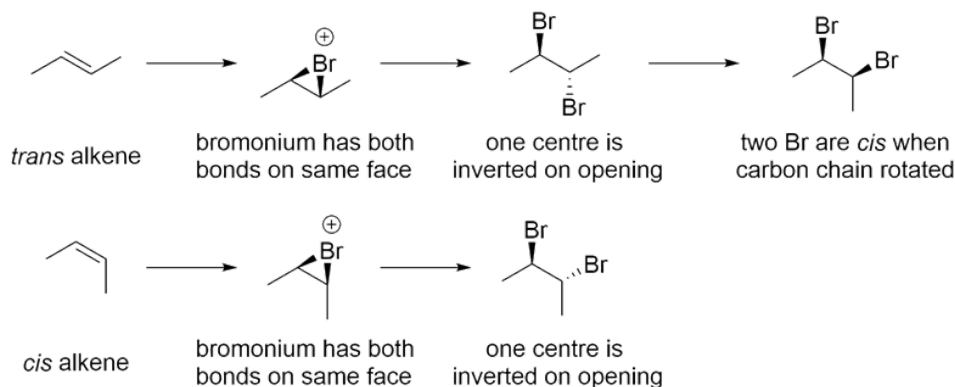
(g) There are many possible chloroalkanes of formula $C_{12}H_{24}Cl_2$. The important clues here are that **B** was formed as a racemic mixture of two enantiomers and that **A** was chosen to be as simple/cheap as possible. Although we do not know the exact mechanism of the reaction, let's assume it is not stereospecific. The simplest/cheapest alkenes are terminal monosubstituted alkenes as there are no isomers to consider. Upon addition of Cl_2 across simple terminal monosubstituted alkenes, only the internal carbon becomes a stereocentre, so the best guess is the straight chain terminal alkene for **A**, and corresponding addition product of this **B**. The one stereocentre is marked with an *.



(h) There are 16 possible isomers. These consist of six pairs of enantiomers and four achiral diastereomers. The isomers have been drawn in such a way to show their maximum possible symmetry. Planes of symmetry have been shown by red lines.



(i) In a bromination reaction, the two bonds to the intermediate bromonium ion first form on the same face of the alkene. The bromide anion then attacks in at one of the two carbon atoms and inverts the stereochemistry of that centre only. Drawing the **HBCD** isomers in the way shown previously (to highlight any symmetry) has the carbon backbone in a *cis* conformation, rather than the more usual *trans*/staggered conformation. Thus, as drawn, when two Br are on the same face (*cis*) this must have come from a *trans* alkene, and when the two Br are on the opposite faces (*trans*) this must have come from a *cis* alkene.



HBCD

All *cis*

cis, cis, trans

cis, trans, trans

All *trans*

Starting alkene

All *trans*

cis, trans, trans

cis, cis, trans

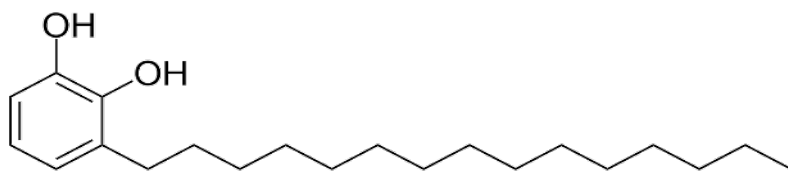
All *cis*

(j) No, it is not possible to tell which alkene was used as both the *cis, cis, trans*, and the *cis, trans, trans* alkenes give three different diastereomers as products. The commercial **HBCD** product is a mixture of the isomers coloured in pink, as the starting alkene is predominantly *cis, trans, trans*-cyclododeca-1,5,9-triene.

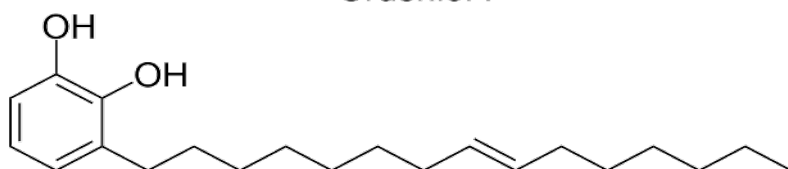


3. Urushiols

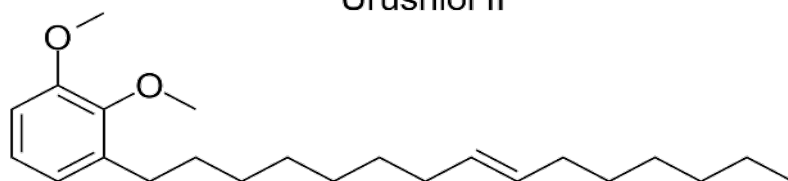
(a)



Urushiol I



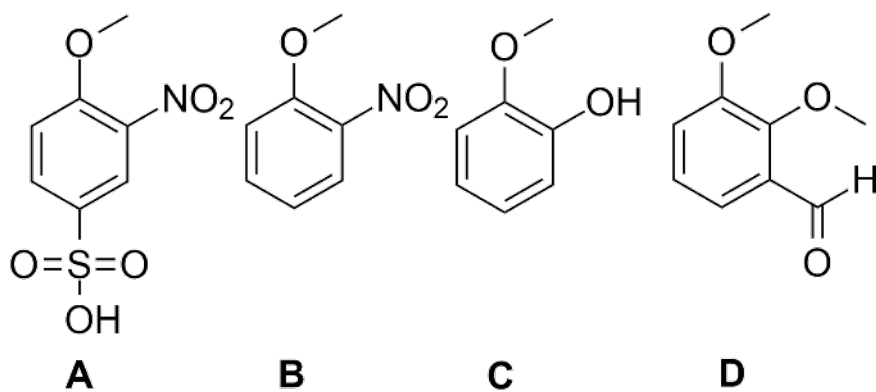
Urushiol II



Dimethylurushiol II

For Urushiol II and Dimethylurushiol II both the *cis*- and the *trans*-isomer would be marked as correct with the given information.

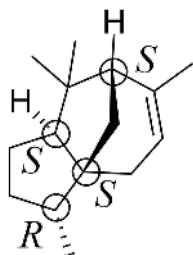
(b)



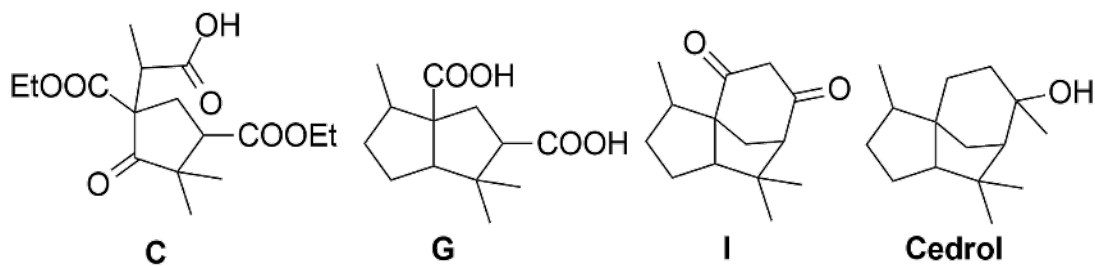


4. Cedrene

(a)

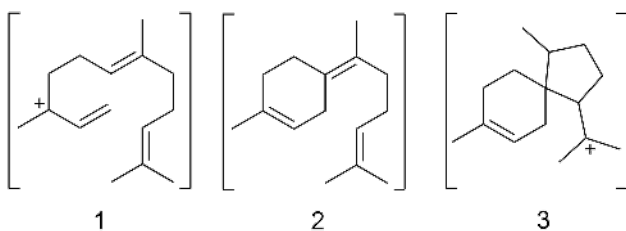


(b)

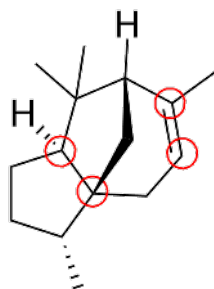


(c) ☒ **Li, NH₃** ☐ LiAlH₄ ☒ **H₂, Pd/C** ☐ HNO₃ ☐ H₂SO₄

(d)



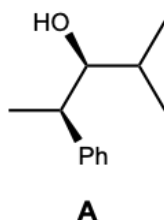
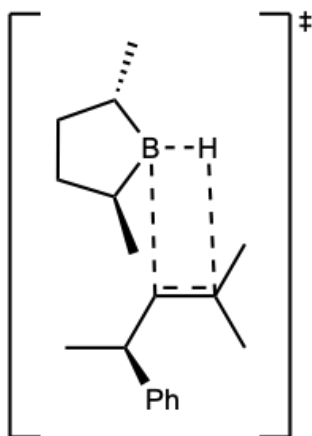
(e)



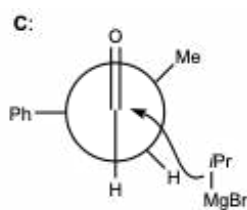
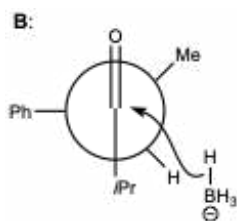


5. Stereochemical models

(a) This is the Masamune hydroboration reaction. Consider the chiral borane approaching from the top versus bottom face of the alkene. The four-membered ring transition state is favoured when the borane approaches from the top.

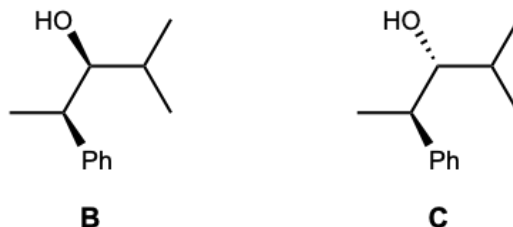


(b)



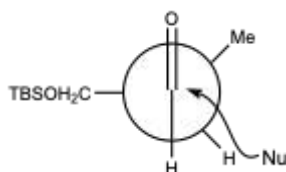


(c)

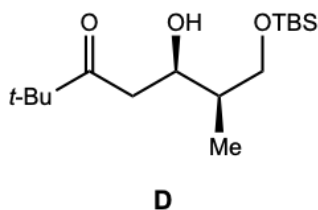


(d) ☒ **B** ☐ C ☐ Either B or C ☐ Neither B nor C

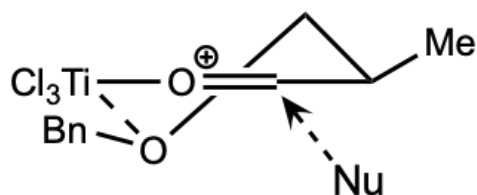
(e)



(f)



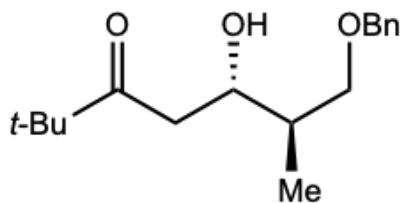
(g)



Nu approaches from the opposite side to Me. The twist boat does not form as the six-membered ring will just open to a lower energy geometry.



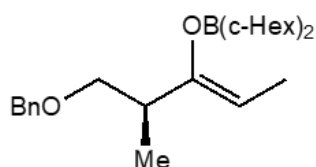
(h)



E

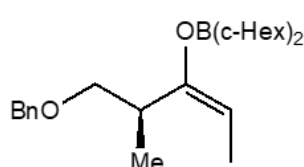
(i) Chelation of the Lewis acid TiCl_4 to both the carbonyl oxygen and benzyl oxygen. The steric bulk of OTBS in the previous case prevents the chelation of TiCl_4 .

(j)



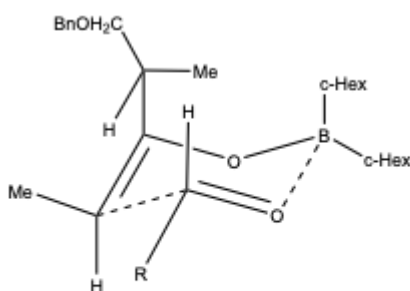
□

(Z) - enolate



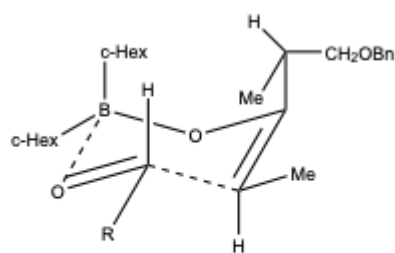
(E) - enolate

(k) There are two possible transition state structures that can be proposed, **X** and **Y**.



X

Suggested by Houk Model



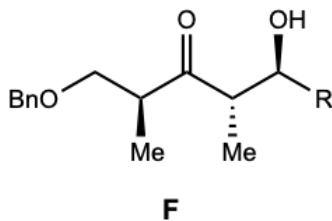
Y

Actual transition state based on experimental product

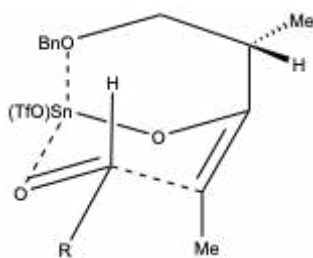
While **X** obeys the Houk model to minimise allylic strain, the transition state **Y** minimises steric strain between H and the large c-Hex groups on Boron and predicts the experimental product **F**.



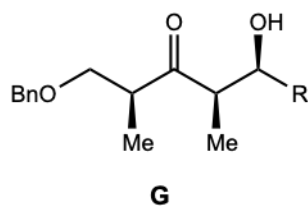
(l)



(m)



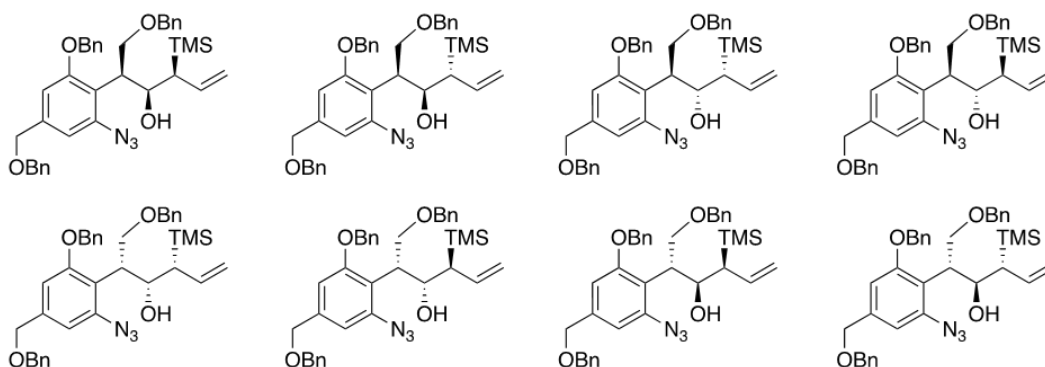
(n)



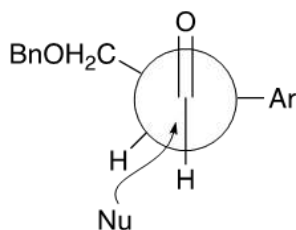


6. Stereocontrol in the synthesis of FR66979

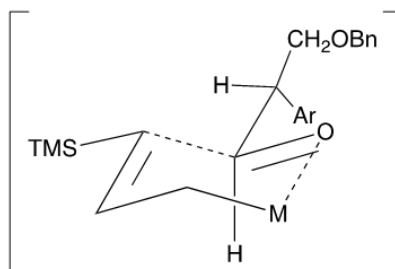
(a)



(b)

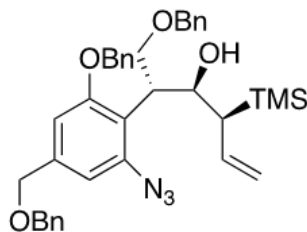


(c)



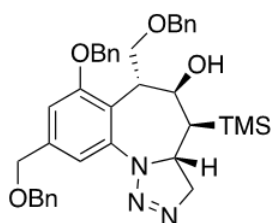


(d)

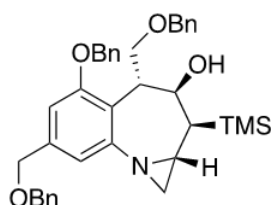


C

(e) Stereochemistry is not required.

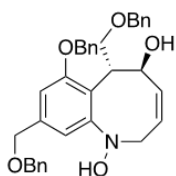


D

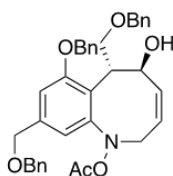


E

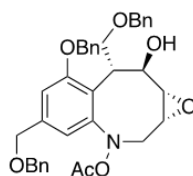
(f) Stereochemistry is not required.



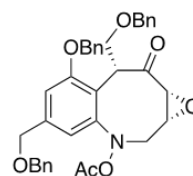
G



H



I

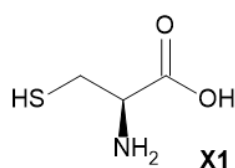


J

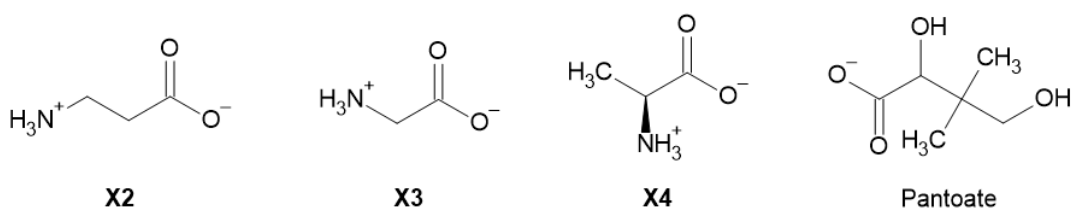


7. Coenzyme A and anaplerotic reactions

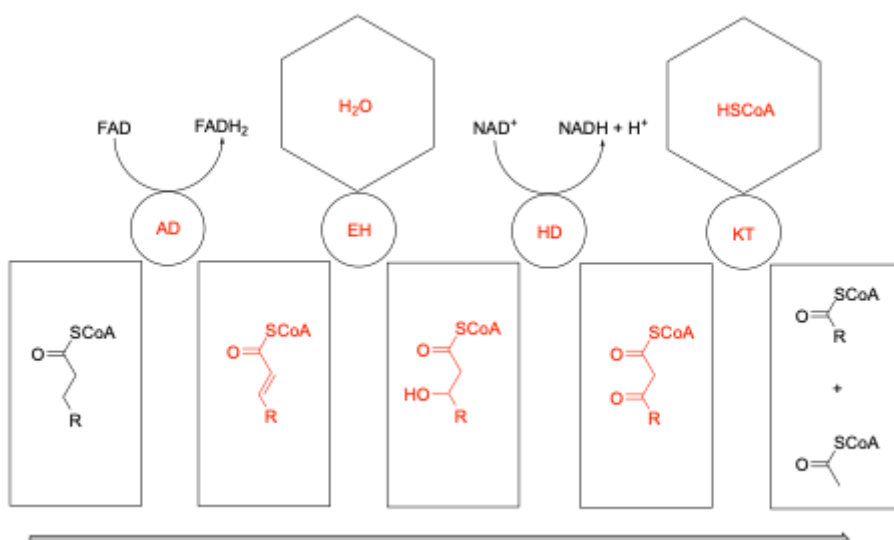
(a) There are two sulfur containing canonical amino acids, cysteine and methionine. Only the former one contains a free thiol group, which is donated to CoA. Thus, **X1** is cysteine. The absolute configuration of the stereocentre in **X1** is *R*.



(b) **X2** is β -alanine, which is a homologue of glycine (**X3**) and structural isomer of alanine (**X4**)



(c),(d),(e)

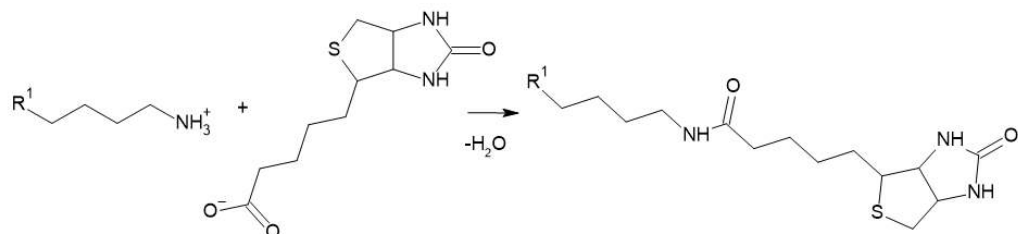


(f) The thiol group is the most readily oxidised one from the given list. The process of $-SH$ oxidation can spontaneously develop in aerobic conditions and does not require co-enzymes or co-factors. Coenzyme A can protect the thiol groups from irreversible oxidation by forming intermolecular S-S bridges.

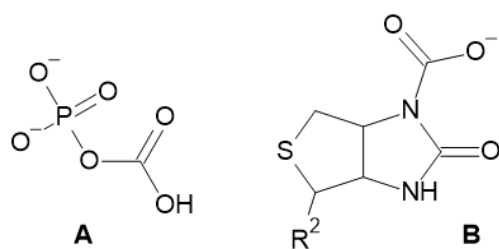


(g) Ligase. E₁ is pyruvate carboxylase.

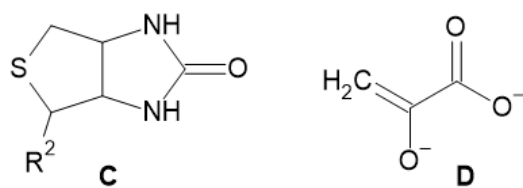
(h)



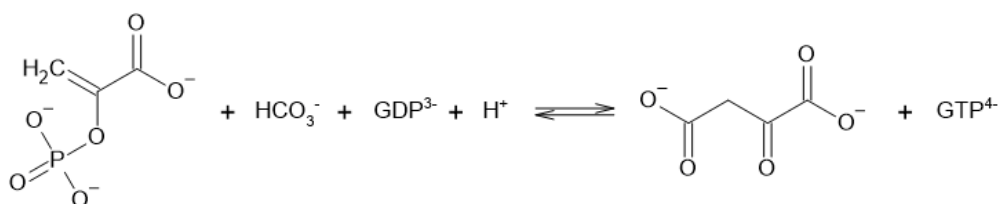
(i)



(j)



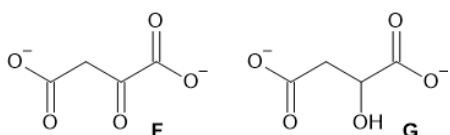
(k)





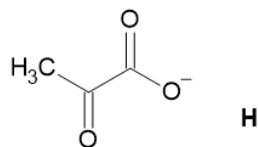
(l) The reverse reaction suggests that E_2 is a lyase, phosphoenolpyruvate carboxykinase. Since phosphoenolpyruvate (PEP) is a superhigh energy molecule, the excess energy left over after carboxylation is used to produce GTP. Complete usage of the PEP energy makes the reaction readily reversible.

(m)



(n) Oxaloacetate and malate are also intermediates of the tricarboxylic acid cycle. Formation of malate from fumarate is reversible, which is responsible for partial distribution of ^{14}C between two carboxylic groups, when malate forms back from fumarate again. The carboxylate carbon next to the hydroxyl group in malate is retained in PEP and glucose.

(o)



(p) E_3 is a lyase, phosphoenolpyruvate carboxylase. By contrast to the E_2 catalysed reaction, GTP is not formed as one of the products. Accordingly, the E_3 catalysed reaction is actually irreversible. E_4 is an oxidoreductase, malate dehydrogenase (oxaloacetate-decarboxylating).

(q) E_5 is a kinase. Moreover, two substrates (pyruvate and inorganic phosphate) are phosphorylated because of this reaction, thus E_5 is typically referred to as dikinase or pyruvate, phosphate dikinase.



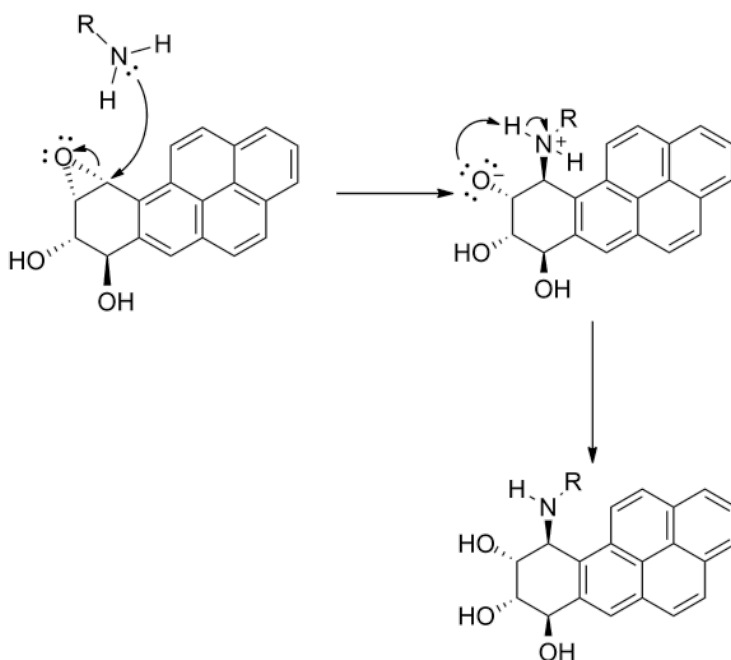
8. Why smoking is deadly

(a) Enzyme 1: Oxidase

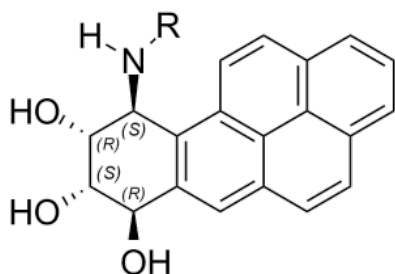
Enzyme 2: Hydrolase

Enzyme 3: Oxidase

(b)

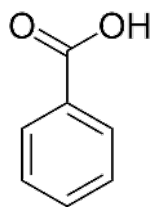


(c)

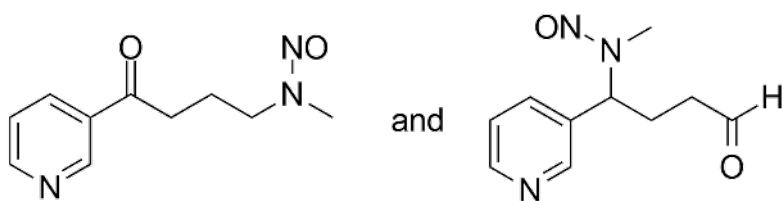




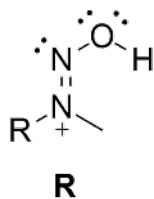
(d) The product is benzoic acid.



(e)

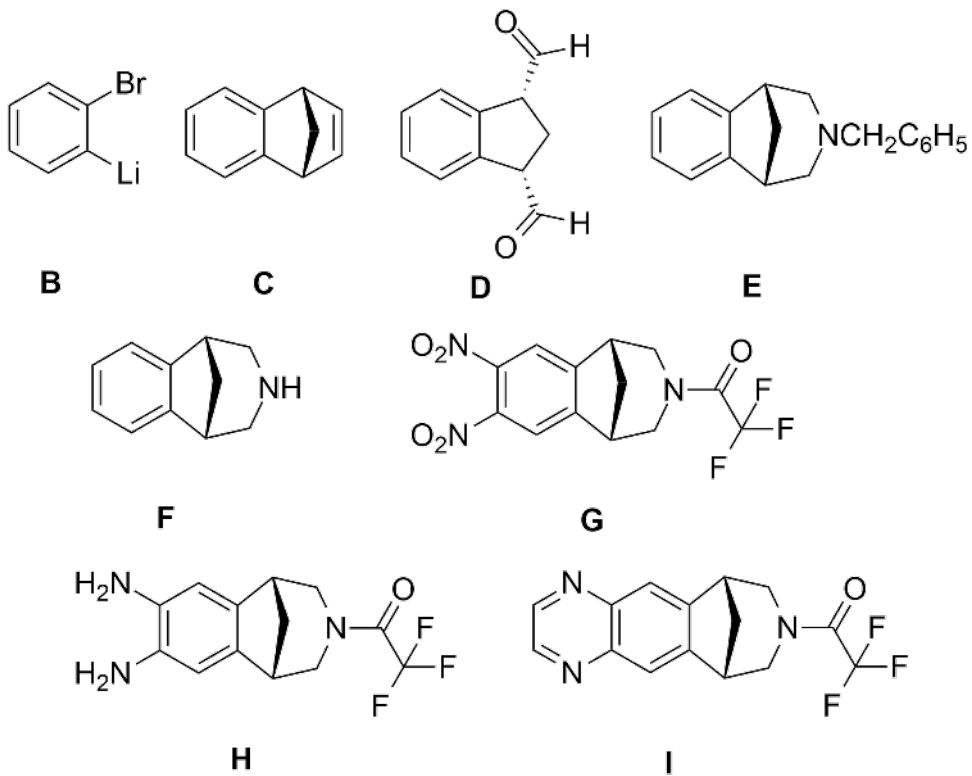


(f)





(g)





9. Determining the stereochemistry of enzymatic reactions

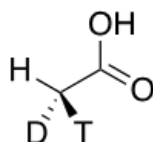
(a) In the original literature, this was performed with the following two steps:

1. O_3

2. I_2 , KI, Na_2CO_3

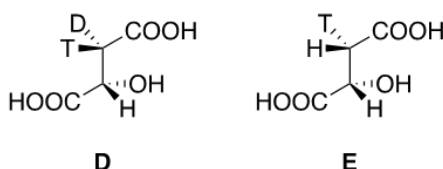
For the purpose of this question, any solution that suggests ozonolysis (or a more recent equivalent method from the literature) followed by iodine in basic conditions (iodoform reaction) can be accepted.

(b)



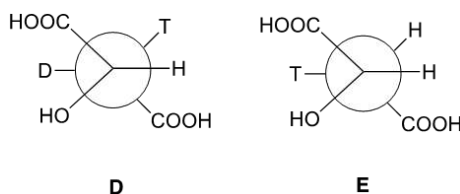
(S)-**B**

(c)



Note that the new stereocentre formed has (*S*)-configuration, and the original stereocentre is inverted. While this is drawn in the most stable conformation of **D** and **E**, a correct answer for this part can be in any conformation.

(d)

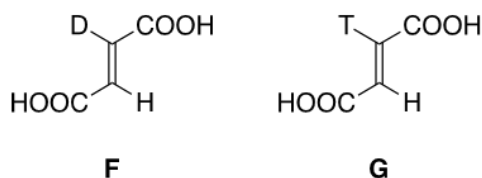


For this part, the Newman projection must be drawn in the most stable conformation, with the two COOH groups *anti* to each other. This helps to



determine which hydrogen isotope is anti-periplanar to OH and gets eliminated as water in the next step.

(e)



(f)

F forms from **D**, and **G** forms from **E**, so **F : G** = 4 : 1

Thus, 80% of T activity will be lost after fumarase (as T is eliminated from **D** to **F**).

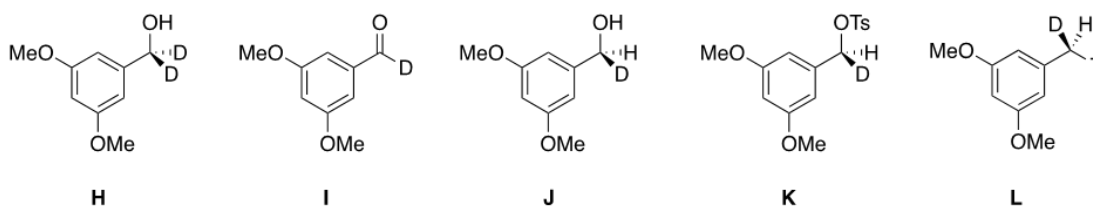
For (*S*)-**B**, **Z** = 0.2

(g)

Similar analysis can be performed. Alternatively observe the symmetry of the system.

For (*R*)-**B**, **Z** = 0.8

(h)



(i)

There are multiple possible methods:

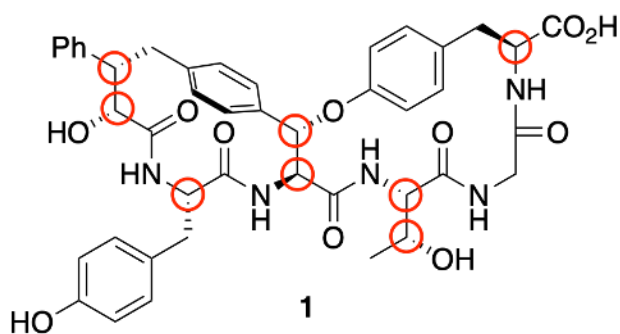
- 1) Use (–)- α -pinanyl-9-BBN.
- 2) Use deuterated (+)- α -pinanyl-9-BBN.

Other reasonable methods can be accepted.

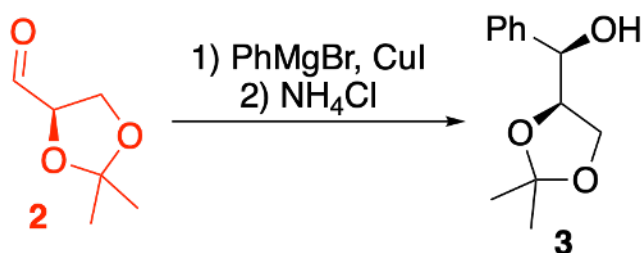


10. The synthesis and derivatisation of natural products

(a)



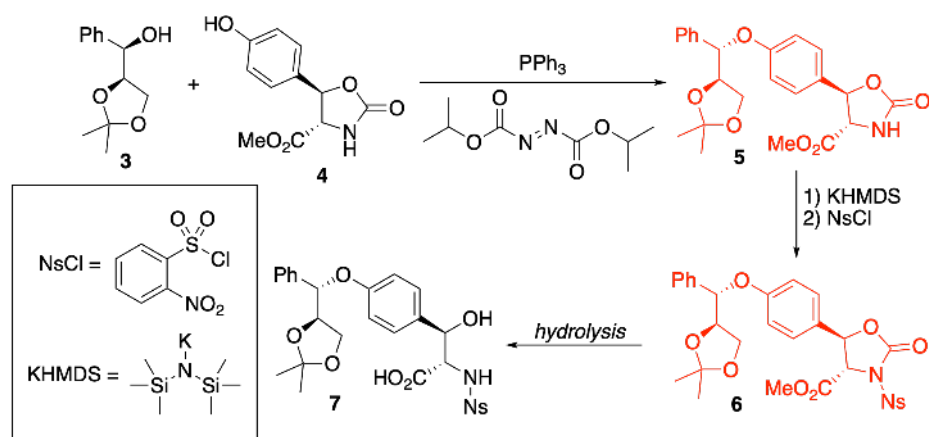
(b)



(c)

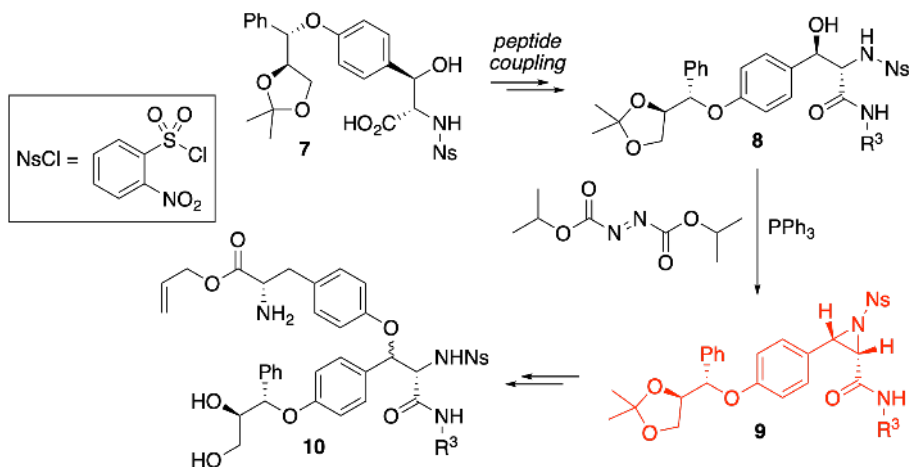
b. Felkin-Anh model with chelation

(d)





(e)

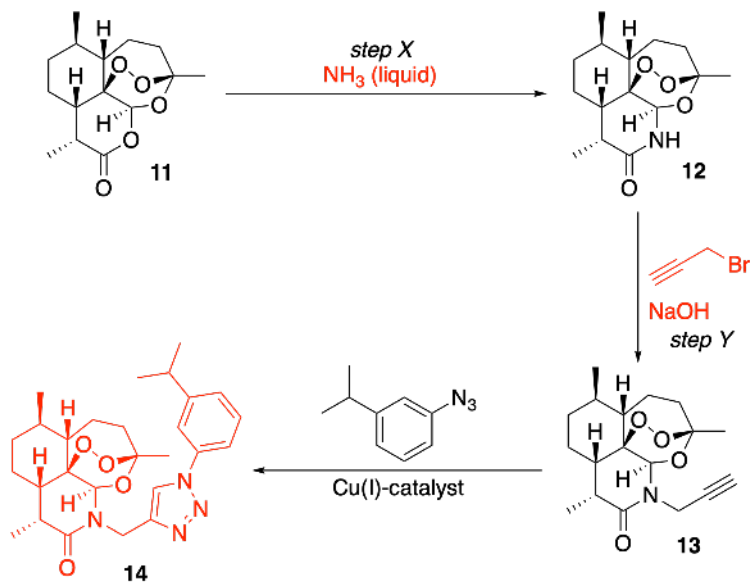


(f)

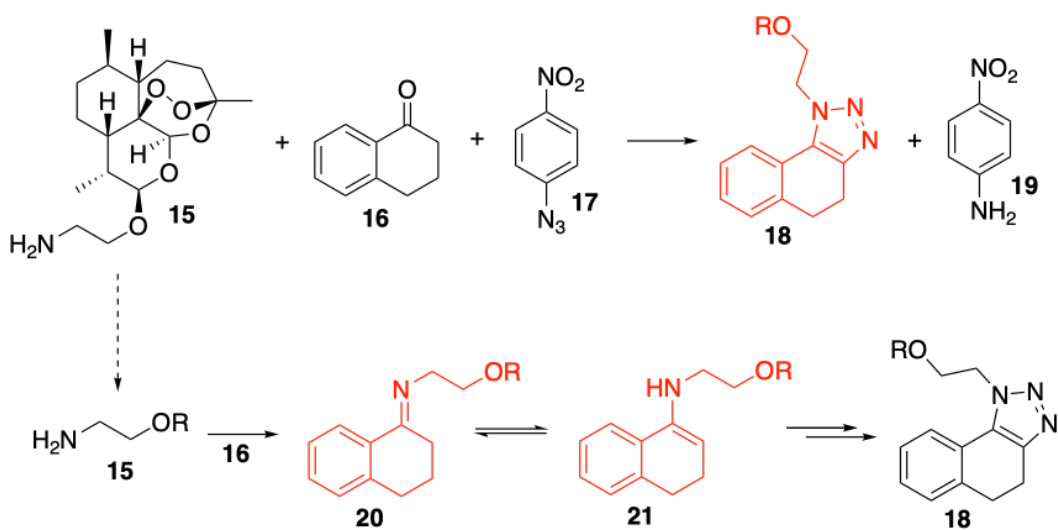
Reagent	Step	Reagent	Step
NMe ₄ Cl, H ₂ O		Br-CH ₂ -CH=CH ₂ , NaOH	
NH ₂ OH		Br-CH ₂ -CH=CH-Br, NaOH	
NH ₃ (liquid)	X	Br-CH ₂ -CH=CH-Br, NaOH	
NH ₂ NH ₂		Br-CH ₂ -C≡CH, NaOH	Y



(g)



(h)

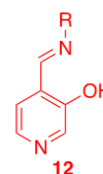
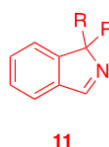
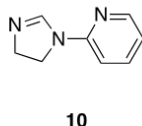
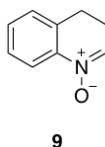
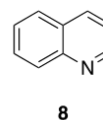
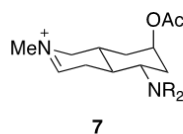
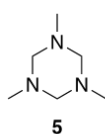
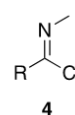
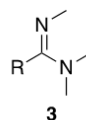
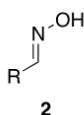
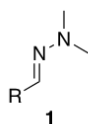




11. A saga about imines

Episode IV: A new imine

(a) Compound **1** is a hydrazone; **2** is an oxime; **3** is an amidine; **4** is an imidoyl chloride; **5** is a heterocycle hexahydrotriazine (an aminal); **7** is an iminium cation; **8** is the aromatic heterocycle quinoline; **9** is a nitron or an imine N-oxide; **10** is a substituted pyridine and dihydroimidazole (amidine). The rest of the compounds are imines (highlighted in red).



(b)

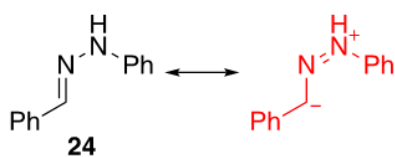
13	14	19	20
19	20	21	22



(c)



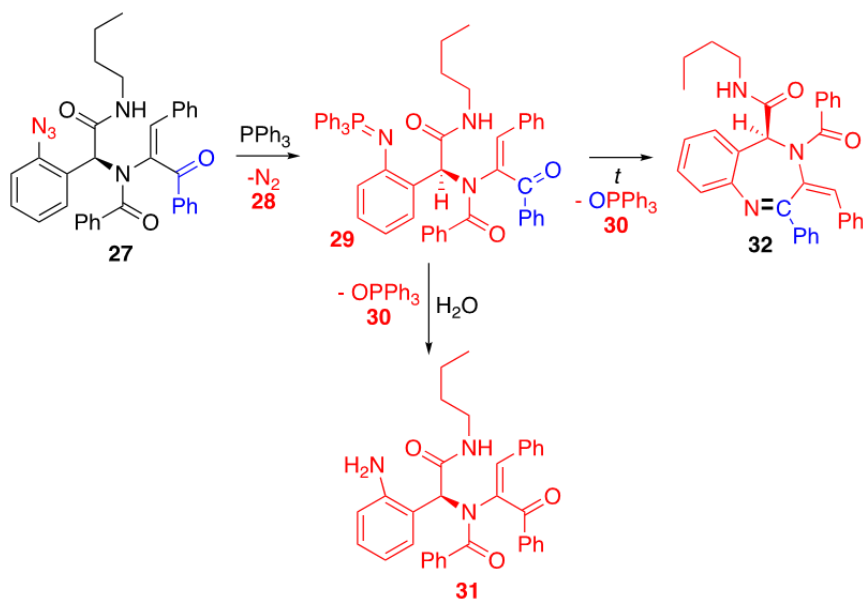
(d)



(e)

Condition(s) for 25 : AB	Condition(s) for 26 : B
--	---------------------------------------

(f) Compound **27** should have azido-group because it reacts with acetylene by copper catalyzed click reaction.

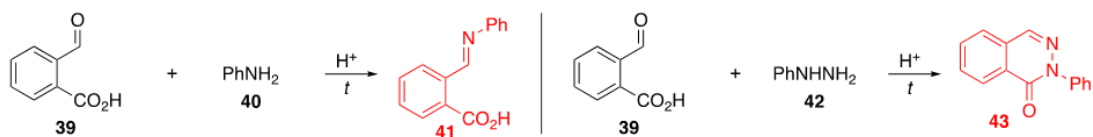




(g)

33: D
34: BEF
35: CF
36: CF
37: CF
38: CF

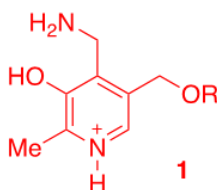
(h)



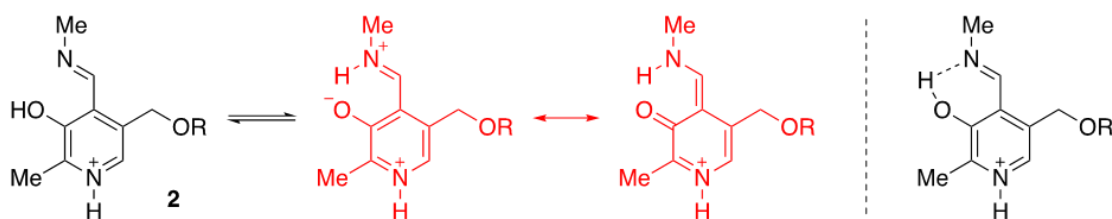


Episode V: The iminium salts strike back!

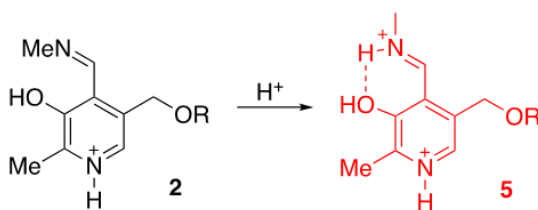
(i) Amines are usually more basic compared with imines. Nitrogen atoms with sp^3 -hybridisation usually possess higher basicity than sp^2 -hybridised nitrogens in the same environment.



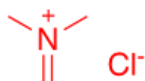
(j) The phenolic proton is very acidic due to the protonated state of pyridine.



(k) Compound **5** is the more favourable reaction outcome: hydrogen bonding stabilises the C=N bond configuration.

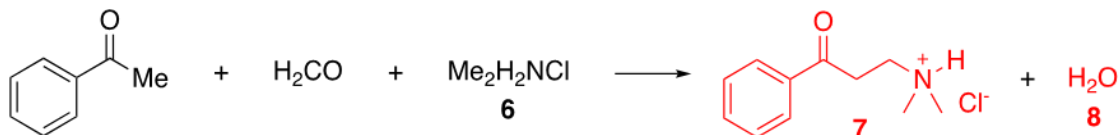


(l)



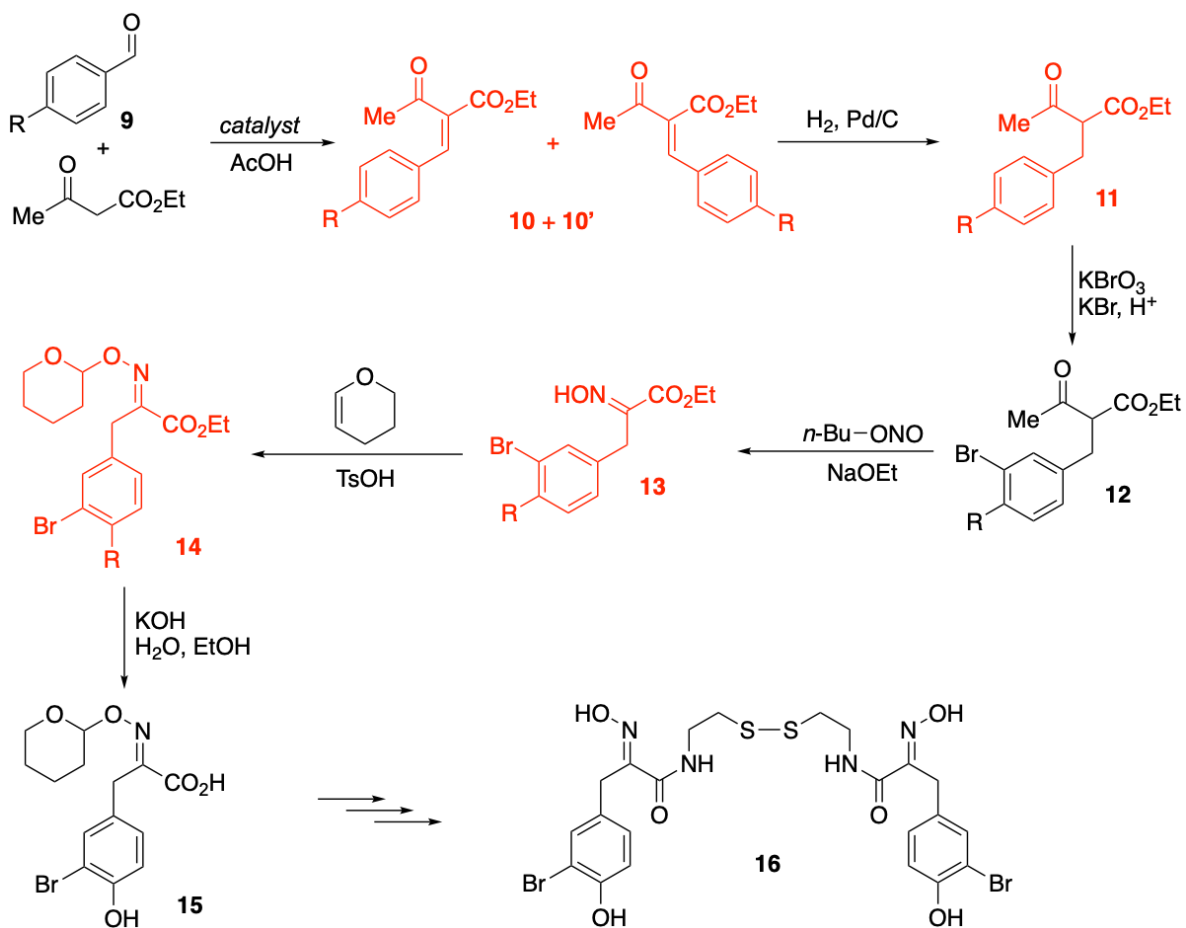


(m)



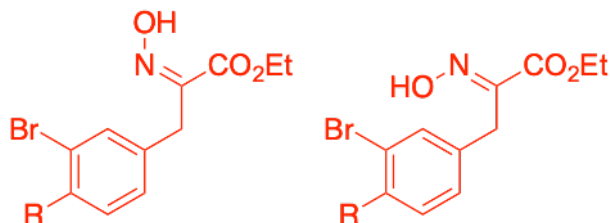
(n) R = OH

(o)

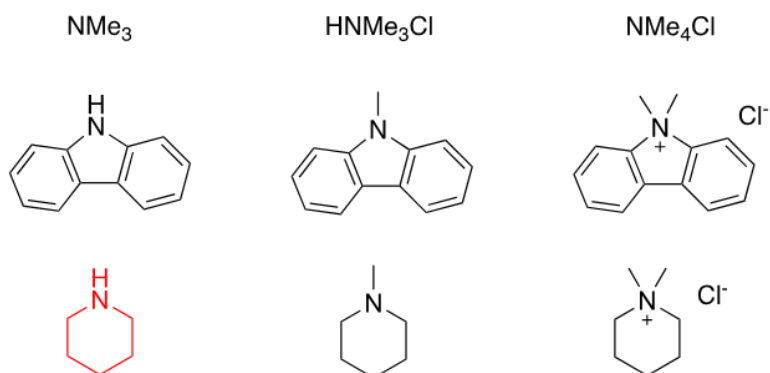




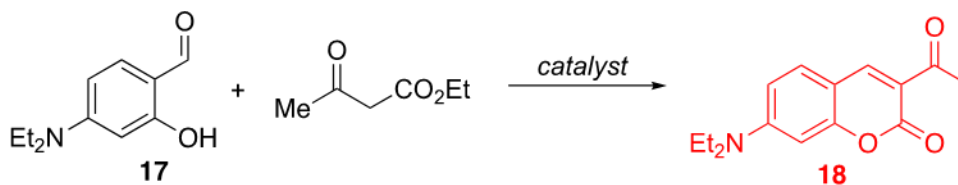
(p)



(q) It is an example of a Knoevenagel condensation.



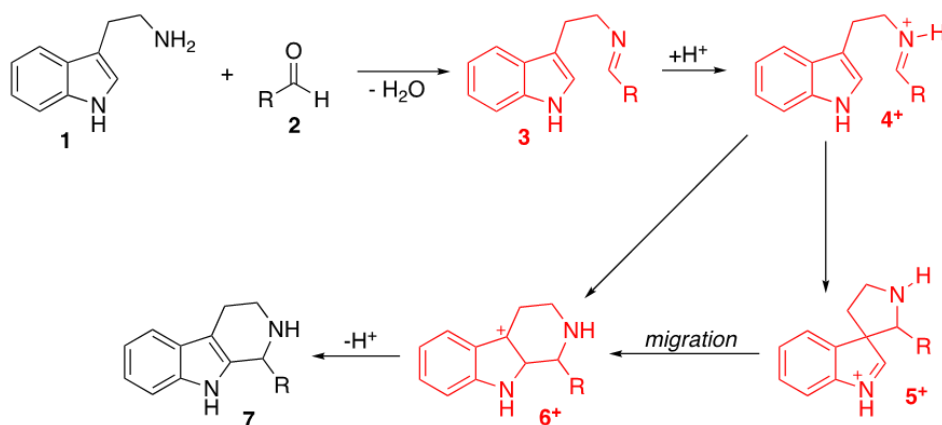
(r) Cyclisation is the reason why only one product is formed in this case.



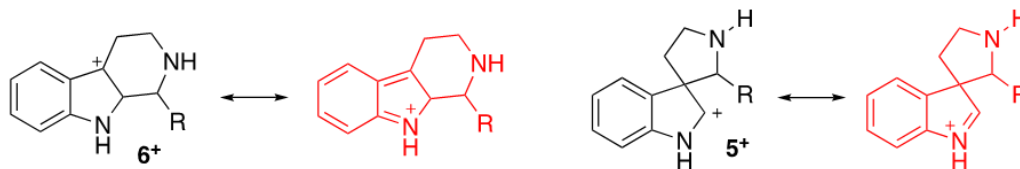


Answer - 12. Imine`s guide to the biochemical galaxy

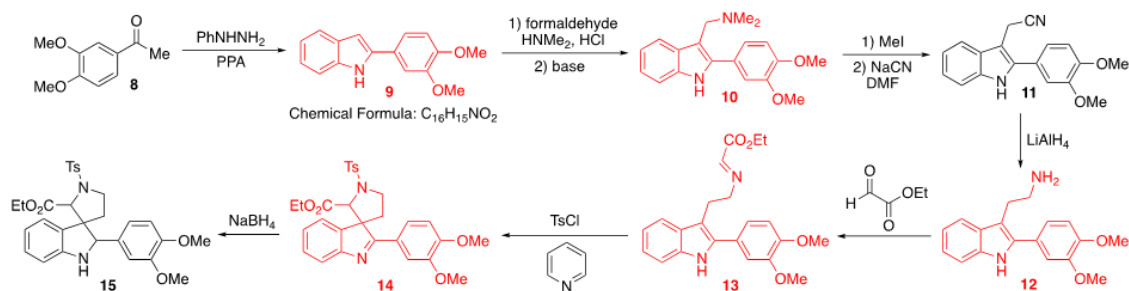
(a) Cations 4^+ and 5^+ are iminium salts discussed in the previous task.



(b)



(c)



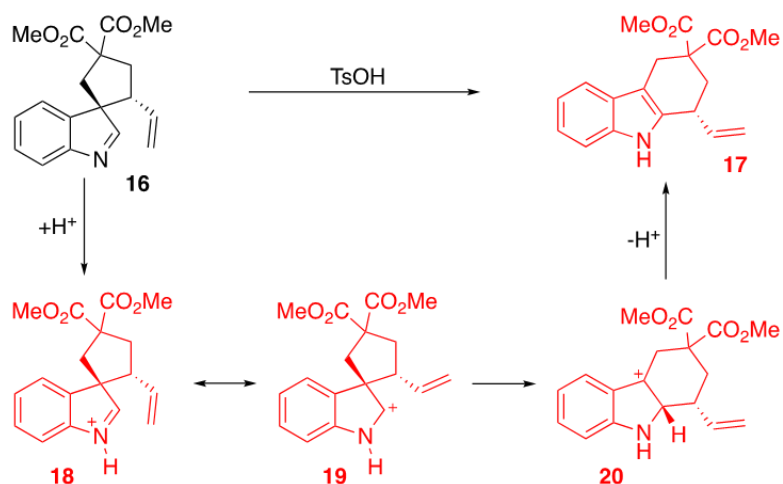


(d)

- A. Aromatisation is favourable.
- B. Aromatisation is unfavourable.
- C. Aromatisation is possible.
- D. Aromatisation is impossible.**
- E. Deprotonation is possible.
- F. Deprotonation is impossible.**
- G. Steric hindrance enhances the rate of six-membered ring formation.
- H. Steric hindrance decreases the rate of six-membered ring formation.**

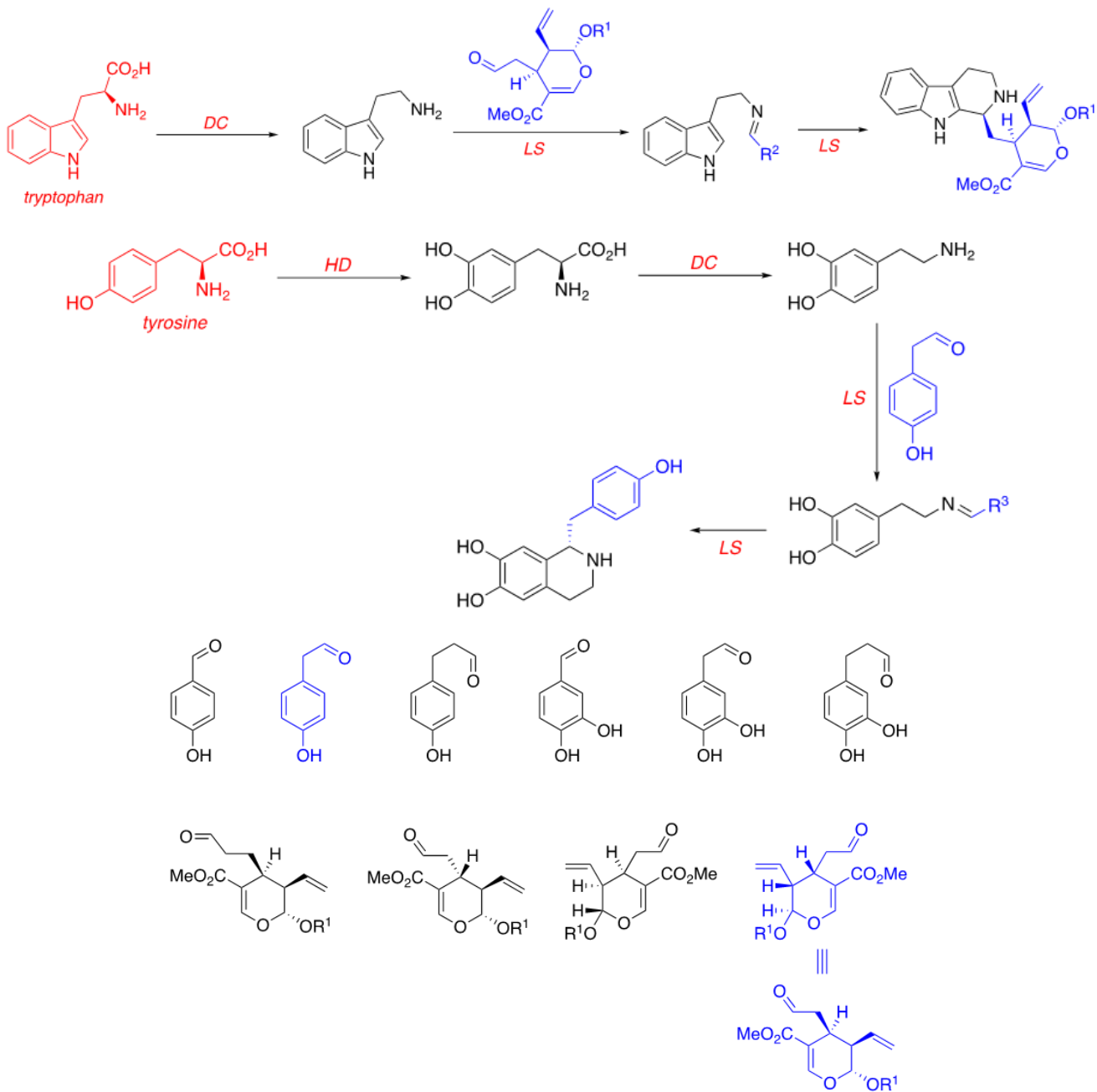
(e) Compound **15** has three stereocenters, which means $2^3 = 8$ stereoisomers.

(f)





(g)

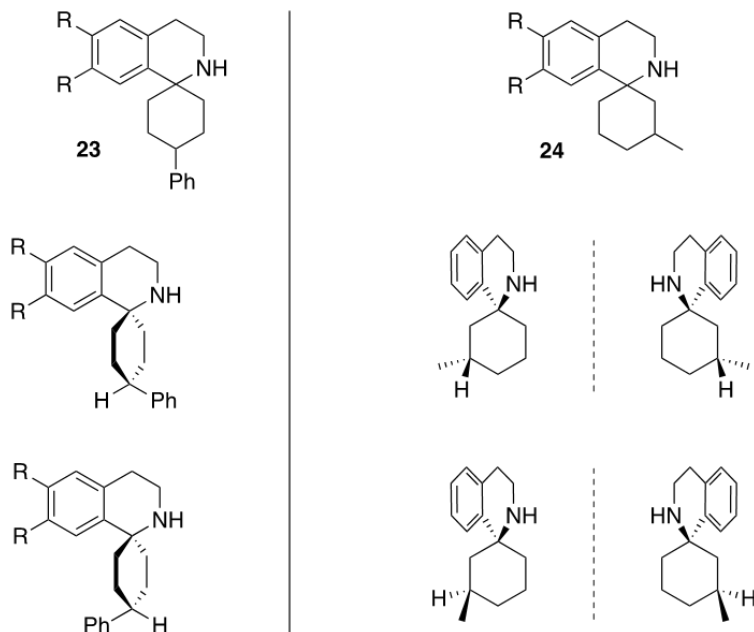




(h) The number of stereoisomers for **23**: **2**

The number of stereoisomers for **24**: **4**

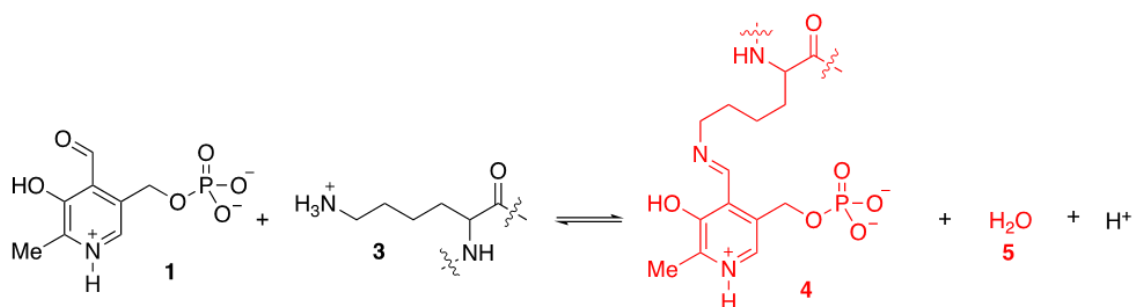
There are two achiral diastereomers for **23**. Compound **24** has two chiral diastereomers (i.e, two pairs of enantiomers or four stereoisomers in total).



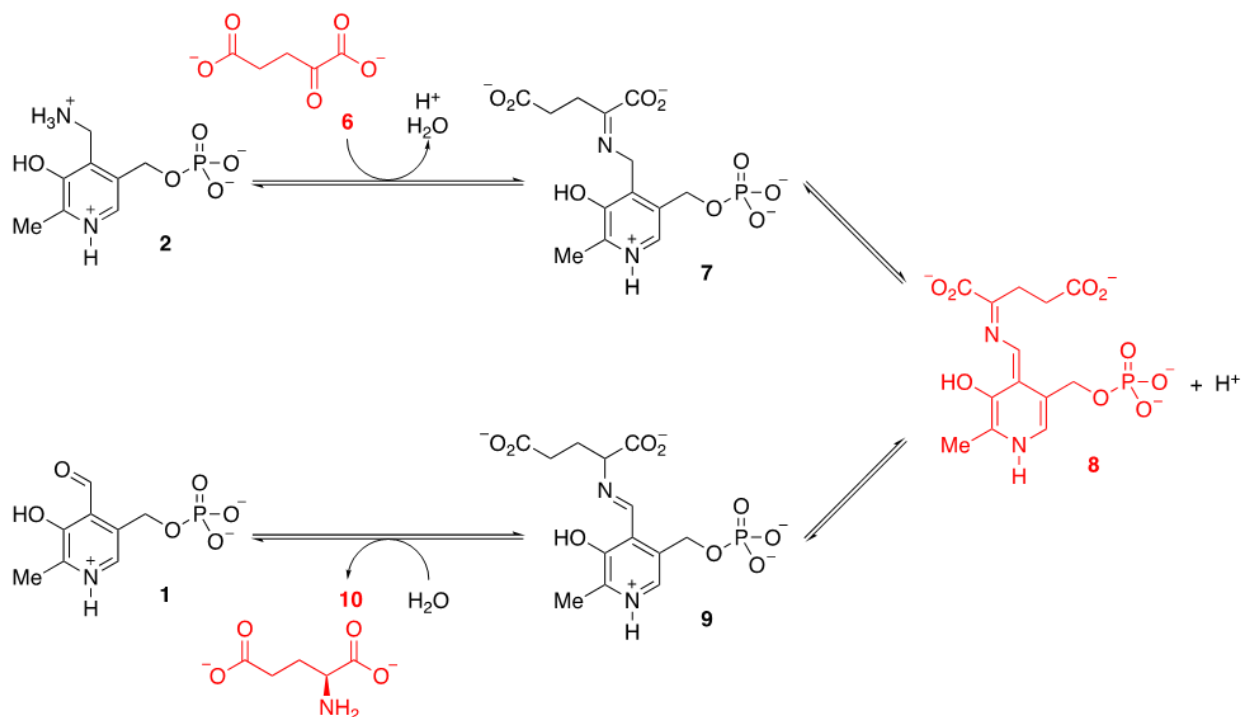


13. Schiff bases, the Universe, and biochemistry

(a)

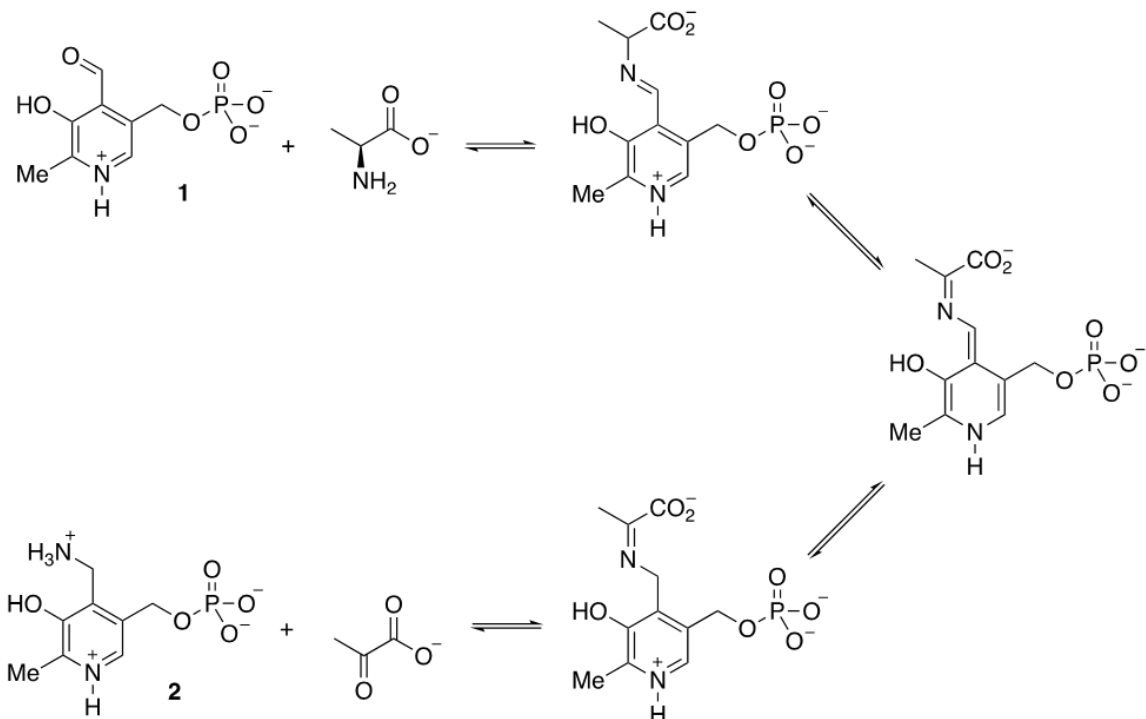


(b) E1 is alanine amino transferase or alanine transaminase (ALT).





(c)



(d) (c) Being electron deficient, the pyridinium ring withdraws electron density from the α -carbon atom.

This leads to elimination of one of its substituents.

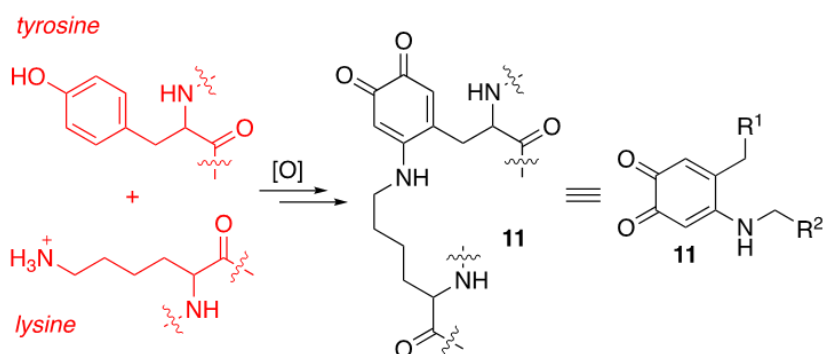
(e)

Reaction type	Initial Schiff base	Quinoid intermediate	Reaction product(s)
a)			 + PLP
b)			 + PLP



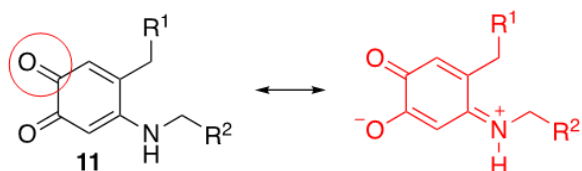
(f)

- a) Alanine
- b) Arginine
- c) Asparagine
- d) Glycine
- e) Methionine
- f) Tyrosine
- g) Tryptophan
- h) Lysine

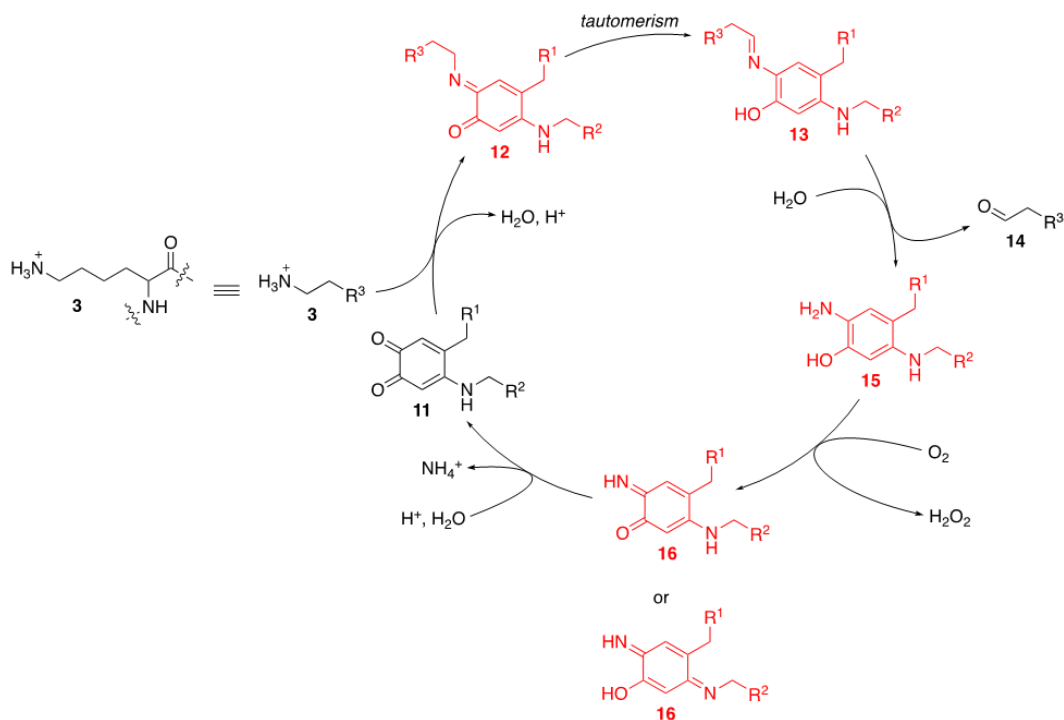


E₂ is lysyl oxidase (LOX).

(g)



(h) **12** is the product of Schiff base formation between lysine residue **3** and the most reactive carbonyl group of the co-factor. Migration of the double bond with subsequent hydrolysis affords the allysine residue. The reduced form of the co-factor is oxidised, and then the imine is hydrolysed which terminates the cycle.

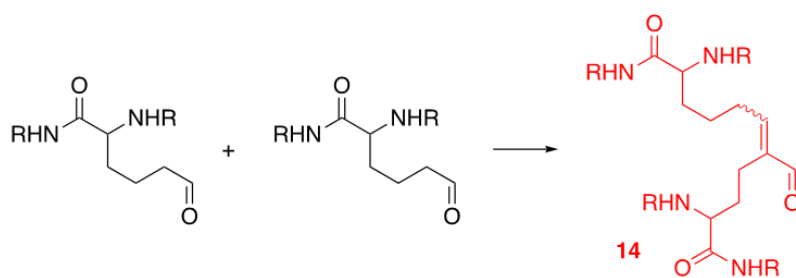
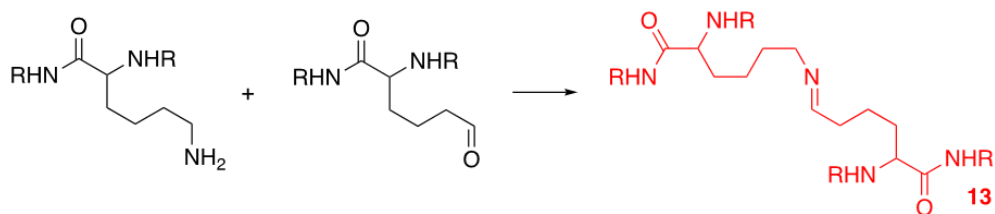


(i)

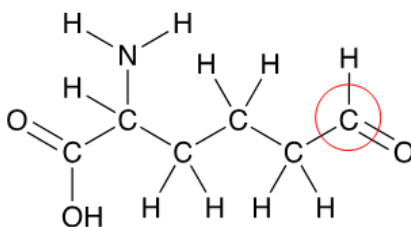
Spectrum number	Molecular ion [M+H] ⁺	Compound
1	145	
2	146	
3	147	regular lysine
4	148	22, 23, 25, 27, 28, 30, 31
5	149	24, 26, 29
6	150	



(j)

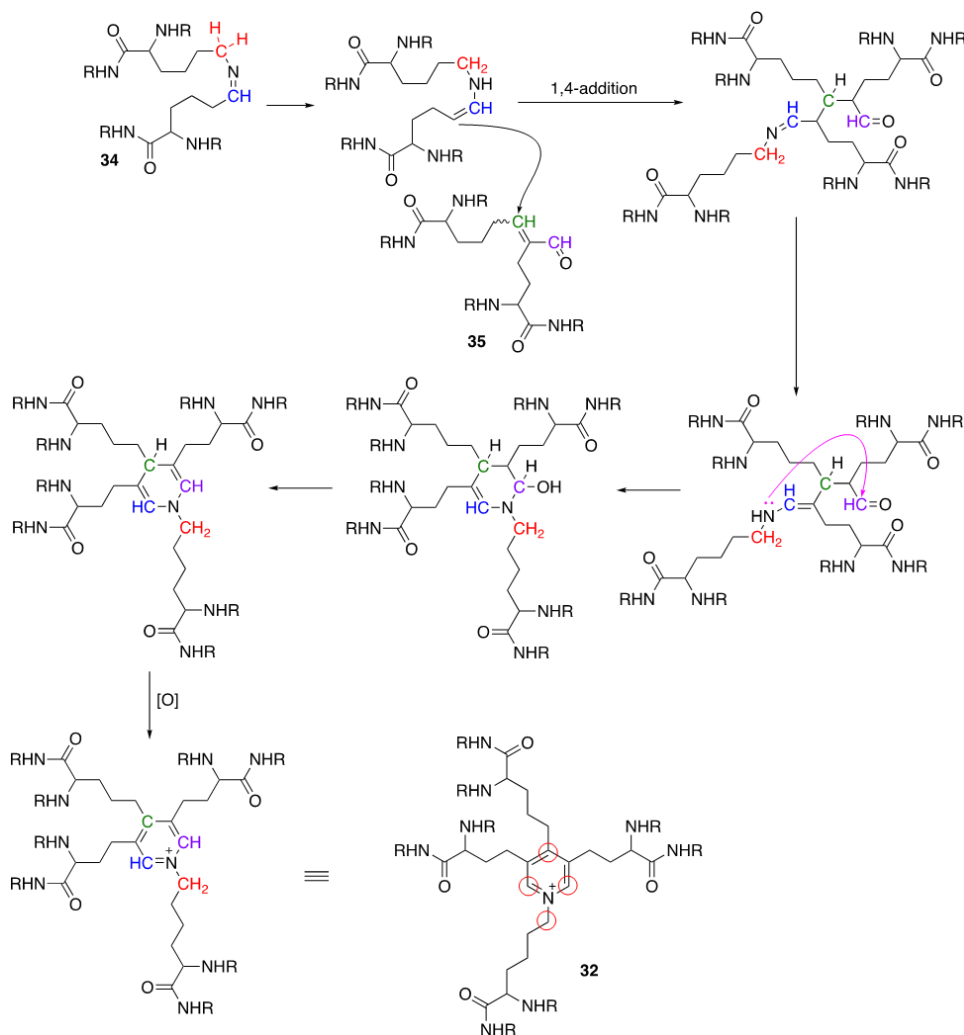


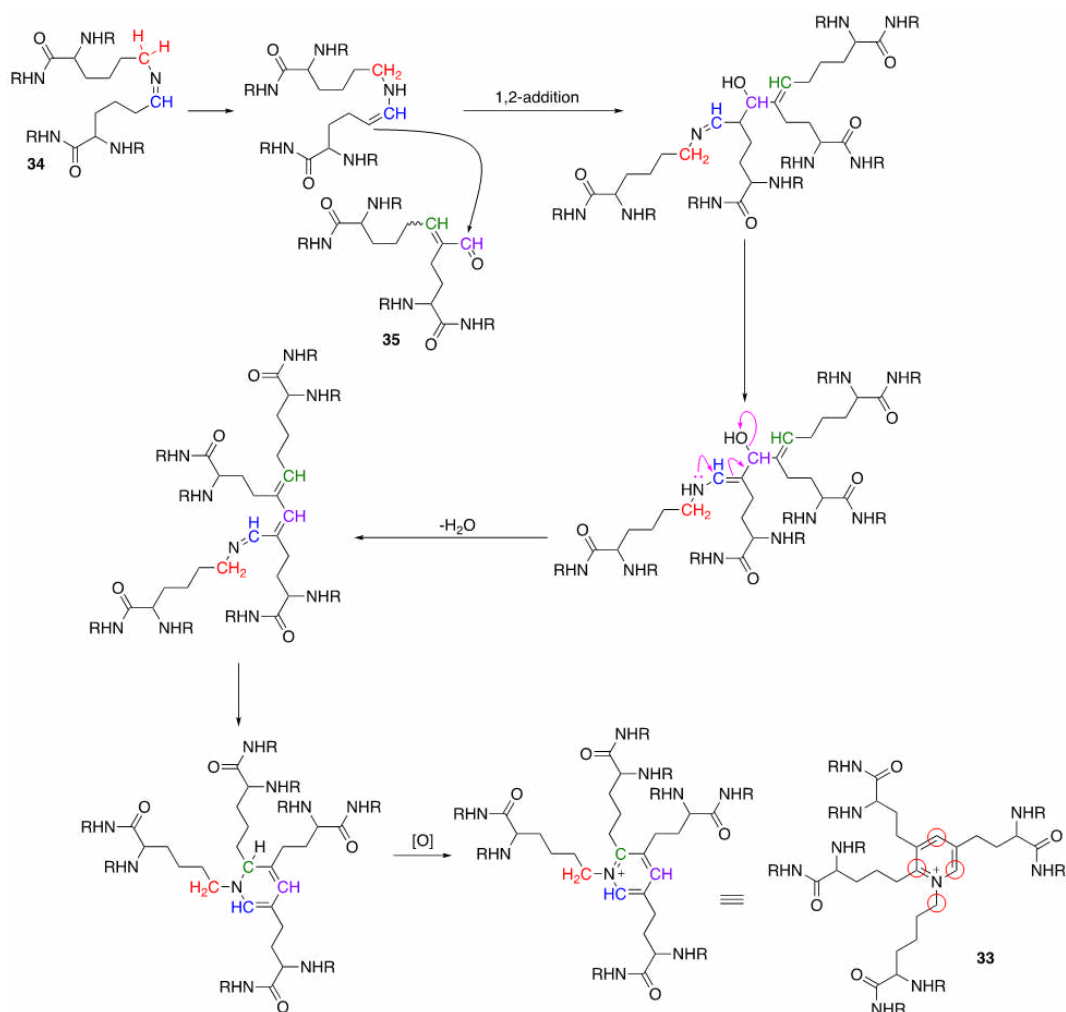
(k)





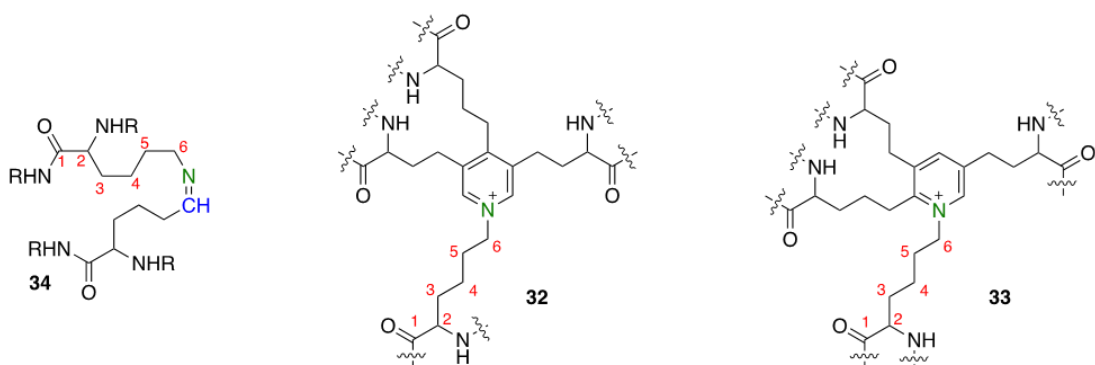
(I) There are several ways to assess this problem. The first option is to trace the carbon atoms in the ring formation mechanism as shown below.



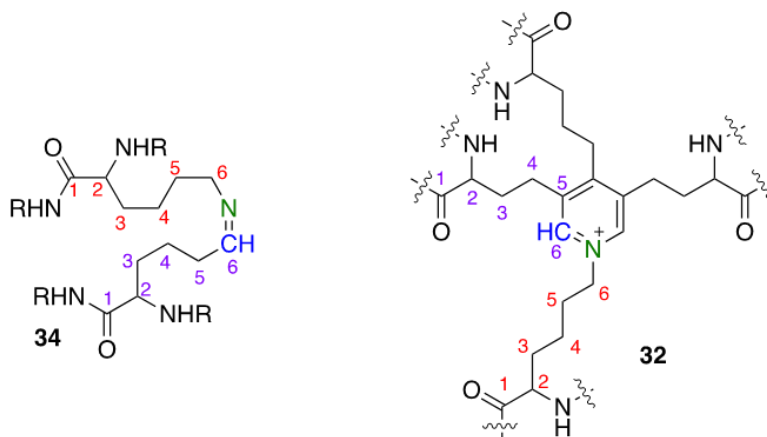


The second option is to know how to count to six. :)

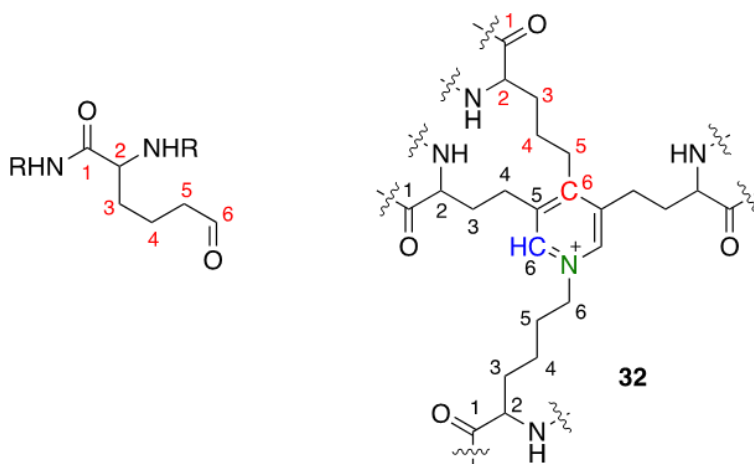
First find a lysine molecule, because there is only one, while there are three allysine molecules. The green nitrogen atom is easy to spot.



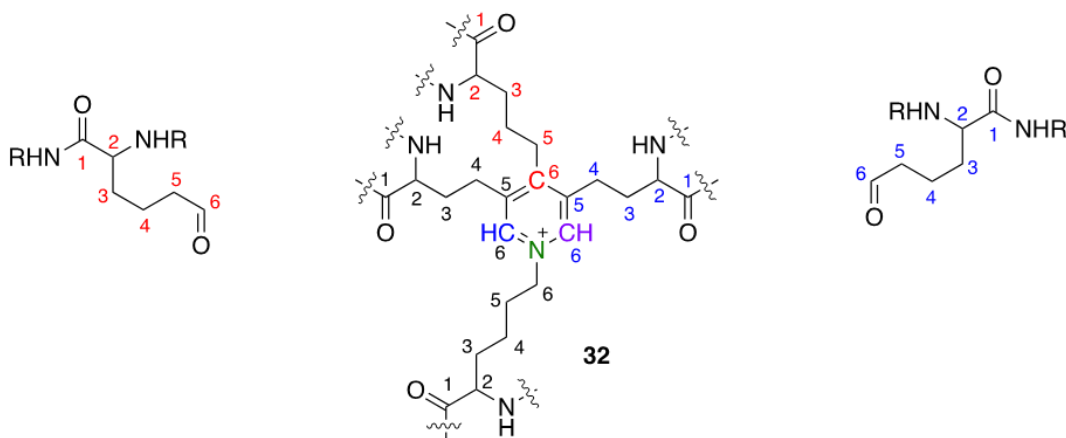
32 is a symmetrical compound. The first allysine is easy to spot by counting to six.



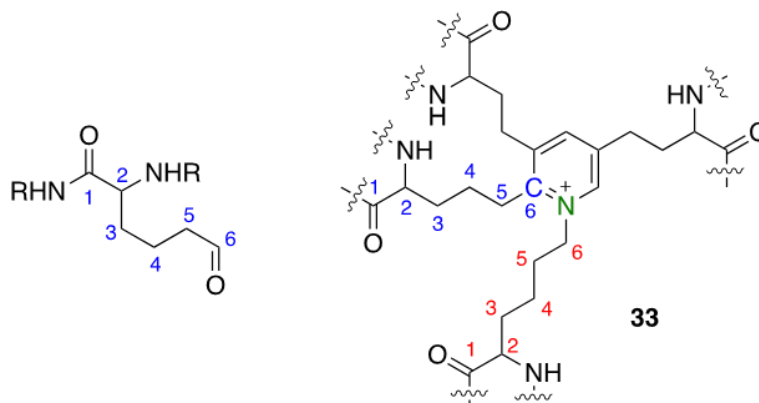
Subsequently, assigning the longer chain numbered in red is more straightforward.



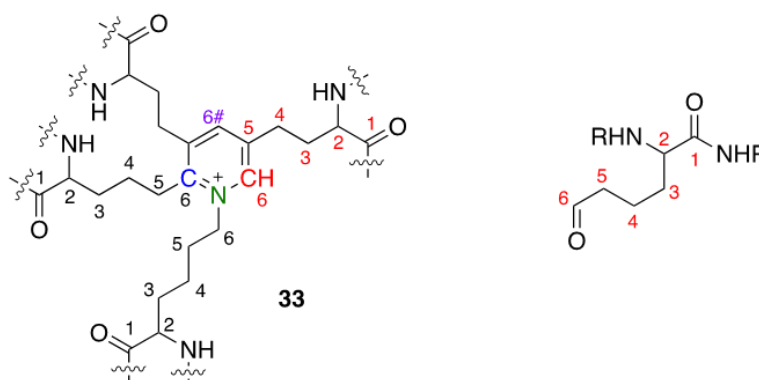
The last allysine is the six carbon atoms left without numbers.



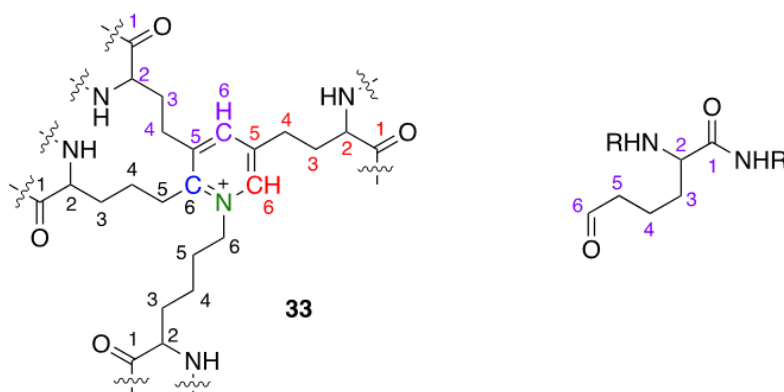
For compound **33**, it is simpler to compare it with allysine itself. The longest chain is found first.



If the right chain is analysed, carbon 6 cannot be left out. When carbon atom #6 is included in this counting, red carbon 6 will have come out of “nowhere”, which is impossible.



The last allysine is the six carbon atoms left without numbers.





14. UAE's driving force

(a) The order of increasing boiling points:

2,2-dimethylbutane	dodecane	pentane-1-thiol	propene	pentan-1-ol	hexane	benzene
2	7	5	1	6	3	4

(b) **X** – S, **A** – H₂S, **B** – SO₂, **C** – S₈

The reaction: $16\text{H}_2\text{S} + 8\text{SO}_2 \rightarrow 3\text{S}_8 + 16\text{H}_2\text{O}$

(c) Sulfur has four stable isotopes: ³²S, ³³S, ³⁴S, ³⁶S.

Peak	256	257	258
<i>I</i> , %	70.40	4.76	25.17

S₈ with a mass of 256 is ³²S₈. Therefore, the probability of this combination of isotopes is $0.9485^8 = 0.6551$ (65.51%).

S₈ with a mass of 257 is ³²S₇³³S. Therefore, the probability of this combination of isotopes is $8 \cdot 0.9485^7 \cdot x$, where *x* is the abundance of ³³S.

S₈ with a mass of 258 is either ³²S₆³³S₂ or ³²S₇³⁴S. Therefore, the probability of this combination of isotopes is $28 \cdot 0.9485^6 \cdot x^2 + 8 \cdot 0.9485^7 \cdot y$, where *x* is the abundance of ³³S and *y* is the abundance of ³⁴S.

The system of equations based on the ratio of intensities in the mass spectrum:



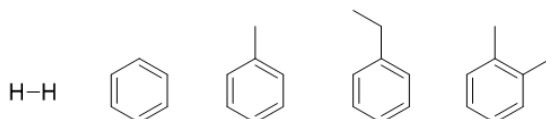
$$\begin{cases} \frac{70.40}{4.76} = \frac{0.9485^8}{8 \cdot 0.9485^7 \cdot x} = \frac{0.9485}{8 \cdot x} \\ \frac{70.40}{25.17} = \frac{0.9485^8}{28 \cdot 0.9485^6 \cdot x^2 + 8 \cdot 0.9485^7 \cdot y} = \frac{0.9485^2}{28 \cdot x^2 + 8 \cdot 0.9485 \cdot y} \end{cases} \Rightarrow \begin{cases} x = 0.0080 \text{ (0.80\%)} \\ y = 0.0422 \text{ (4.22\%)} \end{cases}$$

The total abundance of all four isotopes is 100%, therefore, the abundance of ^{36}S is:

$$1 - 0.9485 - 0.0080 - 0.0422 = 0.0013 \text{ (0.13\%)}$$

(d) There are 2 isomers of butane, 3 isomers of pentane and 5 isomers of hexane. In total, 10 compounds, including the initial linear alkanes (the isomerisation yield is unlikely to be 100%).

(e) Structures of the products (H_2 is also produced in addition to the aromatic compounds):



(f) $\text{C}_{16}\text{H}_{34} \rightarrow$ hexadecane

Cracking: $\text{C}_{16}\text{H}_{34} \rightarrow \text{C}_6\text{H}_{14} + 2\text{C}_5\text{H}_{10}$

Hydrocracking: $\text{C}_{16}\text{H}_{34} + \text{H}_2 \rightarrow 2\text{C}_8\text{H}_{18}$

(g) Structural formulae of **D** (2,4-dimethylpentane) and **E** (2,2,4-trimethylpentane):



(h) **Y** – Pb, **F** – $\text{Pb}(\text{C}_2\text{H}_5)_4$, **G** – $\text{C}_2\text{H}_5\text{Cl}$

The reaction: $4\text{NaPb} + 4\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{Pb}(\text{C}_2\text{H}_5)_4 + 4\text{NaCl} + 3\text{Pb}$



15. In search of an oasis in the desert

(a) The degree of unsaturation of $C_5H_{10}O$ is $(5 \cdot 2 + 2 - 10)/2 = 1$. Therefore, there is either a double bond or a ring. The possible combinations are:

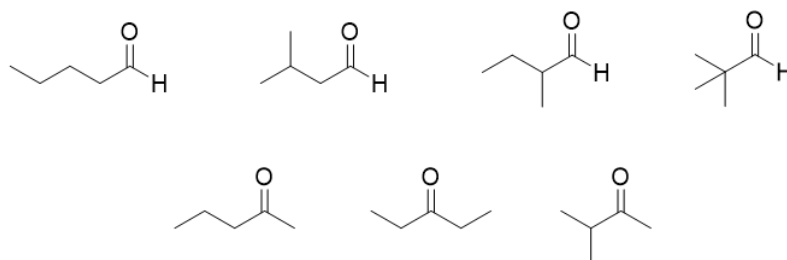
- 1) $-CHO$ (aldehyde)
- 2) $>C=O$ (ketone)
- 3) $>C=C<$ (alkene) + $-OH$ (alcohol)
- 4) $>C=C<$ (alkene) + $-O-$ (ether)
- 5) Cycloalkane (not typically considered as a functional group) + $-OH$ (alcohol)
- 6) Cycloalkane (not typically considered as a functional group) + $-O-$ (ether)
- 7) O-containing heterocycles (cyclic ethers): epoxide/oxetane/tetrahydrofuran

(b) Analysis of IR spectra allows us to determine the functional groups:

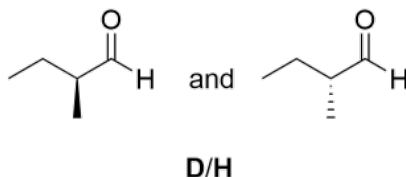
A, C, D, G, H: $1727\text{--}1728\text{ cm}^{-1}$ corresponds to aldehydes

B, E, F: $1717\text{--}1720\text{ cm}^{-1}$ corresponds to ketones

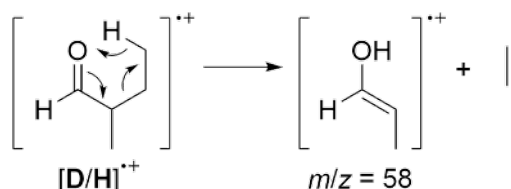
There are only four aldehydes and three ketones with the formula $C_5H_{10}O$:



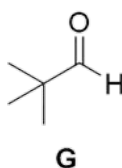
It seems like there should be one more aldehyde. However, if one carefully analyses the data, one can notice that **D** and **H** have absolutely the same data. This could be two enantiomers of the only chiral aldehyde $C_5H_{10}O$, 2-methylbutanal, which can't be distinguished using IR spectroscopy and mass spectrometry:



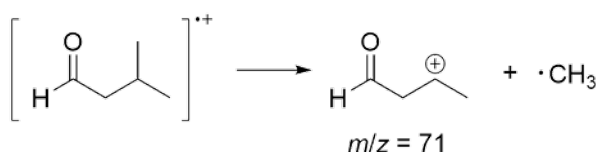
In their mass spectra, the strongest peaks are m/z 29, 41, 57, 58. The peak with m/z 29 is typical for the aldehydes as it corresponds to the HCO^+ produced in a bond cleavage. This peak can also be found in the mass spectra of all other aldehydes **A**, **C**, and **G**. The origin of peaks with m/z 41 (base peak) and 57 is presented in the solution to the next question. The peak with m/z 58 is due to McLafferty rearrangement:



Analysing the structures of the three aldehydes left, one can notice that pentanal and 3-methylbutanal can undergo the McLafferty rearrangement giving the enol radical cation with m/z 44, while 2,2-dimethylpropanal can't. Both mass spectra of **A** and **C** have intense peaks with m/z 44, while the mass spectrum of **G** doesn't. Therefore, **G** is 2,2-dimethylpropanal and the peak with m/z 57 could be assigned to the *tert*-butyl cation (see the answer to the next question for the fragmentation scheme):

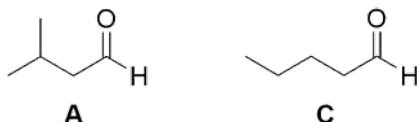


The noticeable difference between the mass spectra of **A** and **C** is the intensity of the peak with m/z 71, which is due to the loss of a methyl group from the molecular ion ($86 - 15 = 71$). In **A**, this peak is of significant intensity, which is more likely for the branched isomer 3-methylbutanal rather than linear pentanal due to the higher stability of the secondary carbocation rather than the primary:

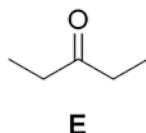




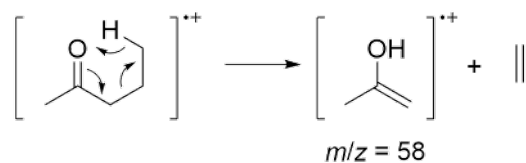
Therefore, the structures of **A** and **C** are the following:



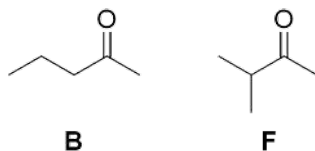
The remaining unknowns are the ketones **B**, **E**, and **F**. The main fragmentation pathway for ketones is bond cleavage producing an acyl cation. In the mass spectra of **B** and **F**, it is CH_3CO^+ (m/z 43), while in **E** it is $\text{C}_2\text{H}_5\text{CO}^+$ (m/z 57). Therefore, **E** is pentan-3-one (see the answer to the next question for the fragmentation scheme):



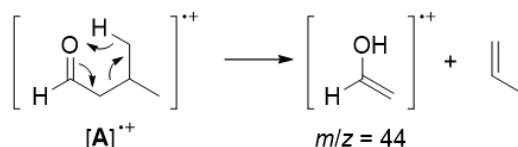
To differentiate between pentan-2-one and 3-methylbut-2-one, that both produce the acyl cation CH_3CO^+ , one can notice that only pentan-2-one has a long enough chain to undergo the McLafferty rearrangement producing the enol radical cation with m/z 58:



This peak is only found in the mass spectrum of **B**. Therefore, **B** is pentan-2-one and **F** is 3-methylbut-2-one:

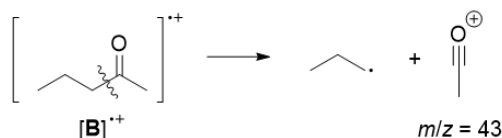


(c) Compound **A** – McLafferty rearrangement:

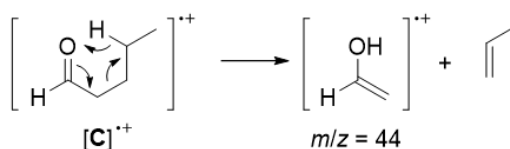




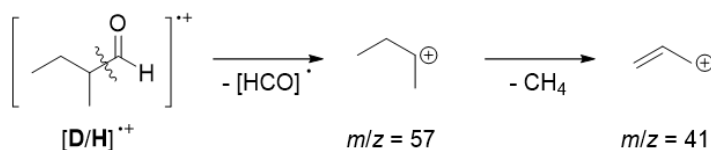
Compound **B** – bond cleavage with the formation of acyl cation (acyl radical has a lower ionisation energy than propyl radical):



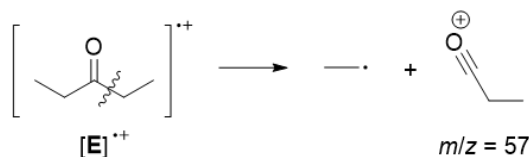
Compound **C** – McLafferty rearrangement:



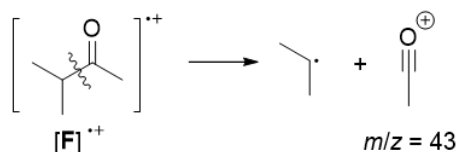
Enantiomers **D** and **H** – sequence of fragmentations forming the allyl cation, most likely:



Compound **E** – bond cleavage with the formation of acyl cation (acyl radical has a lower ionisation energy than ethyl radical as can be seen from the relative intensities of the peaks with m/z 29 (C_2H_5^+) and 57 ($\text{C}_2\text{H}_5\text{CO}^+$):



Compound **F** – bond cleavage with the formation of acyl cation (acyl radical has a lower ionisation energy than propyl radical):





Compound **G** – bond cleavage with the formation of *tert*-butyl cation (*tert*-butyl radical has a lower ionisation energy than formyl radical as can be seen from the relative intensities of the peaks with m/z 29 (HCO^+) and 57 ($t\text{-Bu}^+$):





16. Fullerenes and polyhedra

(a) Each vertex connects to three edges. Each edge connects to two vertices. Therefore, there must be $\frac{3}{2}$ times the number of edges as the number of vertices. Hence, $e = \frac{3n}{2}$.

(b) The known values for v and e can be put into the Euler relationship.

$$\begin{aligned}v + f &= e + 2 \\n + f &= \frac{3n}{2} + 2 \\f &= \frac{n}{2} + 2\end{aligned}$$

(c) Pentagons have five vertices. Hexagons have six vertices. Each vertex is shared by three faces. Therefore, we can say that:

$$\frac{6h + 5p}{3} = v = n$$

We can also relate the number of pentagons and hexagons to the total number of faces and n via the Euler relationship:

$$f = p + h = \frac{n}{2} + 2$$

This gives a pair of simultaneous equations. We can then solve for p and h .

$$\begin{aligned}h &= \frac{n}{2} + 2 - p \\ \frac{6\left(\frac{n}{2} + 2 - p\right) + 5p}{3} &= n \\ \frac{3n + 12 - 6p + 5p}{3} &= n \\ 3n + 12 - p &= 3n \\ \mathbf{p} &= \mathbf{12} \\ h &= \frac{n}{2} + 2 - 12 \\ \mathbf{h} &= \mathbf{\frac{n}{2} - 10}\end{aligned}$$

(d) Dodecahedron. Students should recognise the dodecahedron as one of the five Platonic solids. All 12 faces are regular pentagons. Note that C_{20} is predicted as the



smallest possible fullerene. Structures where two pentagons share an edge have increased bond angle strain and in C_{20} all edges are shared by two pentagons making it a very strained structure.

(e) These can be derived from the figures in the question and the equations.

(a,b)	$v = n$	e	f	h
(1,1)	60	90	32	20

(f) These can be derived from the figures in the question and the equations.

(a,b)	$v = n$	e	f	h
(2,0)	80	120	42	30
(2,1)	140	210	72	60
(2,2)	240	360	122	110
(3,0)	180	270	92	80
(3,2)	380	570	192	180

(g) Structure (i) (4,0). Structure (ii) (3,3). Structure (iii) (6,6). Structure (iv) (3,1). Structure (v) (4,3). Structure (vi) (10,6).

These Goldberg polyhedra fall into three classes. The first class can be described as $(a,0)$, i.e., where one of a or b is zero. These structures have planes of symmetry and are achiral. This means that (4,0) and (0,4) are equivalent. Hence, (0,4) should also be considered a correct answer for structure (i). The convention is for b to be zero in these structures. The second class can be described as $a = b$. These structures also possess planes of symmetry and are achiral. The third class are the remaining structures where a and b are not equal and are both non-zero. These structures do



not possess mirror planes and are chiral structures. This means that (3,1) and (1,3) are not the same and are in fact mirror images (enantiomers) of each other. For structures (iv), (v), and (vi) either permutation of numbers can be accepted as *a* and *b* directions have not been specified here. However, it is important to realise that these are different.

(h) (i): The structures (6,0) and (7,0) have different numbers of faces, 362 and 492 faces respectively. The only descriptor that applies here is allotropes.

(ii): The structures (7,0) and (5,3) have the same number of faces (492) and therefore the same number of carbon atoms. They are both allotropes of each other and isomers of each other. They have different connectivity of pentagons and hexagons and so are not stereoisomers.

(iii) Structures (7,0) and (0,7) are exactly the same. A simple rotation converts one into the other. By convention the structure is called (7,0). This structure is achiral as the shape contains planes of symmetry.

(iv) Structures (5,3) and (3,5) are not the same. These structures are enantiomers of each other. These structures do not have mirror planes and are chiral. In addition to being enantiomers of each other, they also fall into the more general class of allotropes, isomers, and stereoisomers.

(i) To determine the relative intensity of peaks we need to consider a statistical factor in addition to just multiplying the abundances together. In $^{12}\text{C}_{60}$ there is only one possible arrangement, so this has a statistical factor of 1. In $^{12}\text{C}_{59}^{13}\text{C}$ there are 60 possible arrangements as each one of the carbons could be the ^{13}C , giving this a weighting of 60. In general, these weightings are given by the mathematical combination function (also known as the binomial distribution or Pascal's triangle). They can be determined from the following equation, for a species with *n* carbons of formula $^{12}\text{C}_x^{13}\text{C}_y$:

$$\text{weighting} = \frac{n!}{y!(n-y)!}$$

$$\text{Amount of } ^{12}\text{C}_{60} = (0.9894)^{60} = 52.761\%$$

$$\text{Amount of } ^{12}\text{C}_{59}^{13}\text{C} = 60 \times (0.9894)^{59} \times (0.0106) = 33.916\%$$

$$\text{Ratio} = 52.761:33.916 = 1.556:1$$

(j)

$$\text{Amount of } ^{12}\text{C}_{70} = (0.9894)^{70} = 47.428\%$$

$$\text{Amount of } ^{12}\text{C}_{69}^{13}\text{C} = 70 \times (0.9894)^{69} \times (0.0106) = 35.568\%$$

$$\text{Ratio} = 47.428:35.568 = 1.333:1$$



(k) For a structure where there are n ^{12}C carbon atoms the statistical weighting is:

$$\frac{n!}{0!(n-0)!} = 1$$

For a structure where there is one ^{13}C and the rest are ^{12}C the statistical weighting is:

$$\frac{n!}{1!(n-1)!} = n$$

For there to be a greater proportion of fullerenes with one ^{13}C than no ^{13}C , we therefore need:

$$\begin{aligned} n \times (0.9894)^{n-1} \times (0.0106) &> (0.9894)^n \\ n &> \frac{0.9894}{0.0106} \\ n &> 93.3 \\ \mathbf{n} &= \mathbf{94} \end{aligned}$$

Remember that fullerenes must have an even number of carbon atoms.

(l) For a structure where there are two ^{13}C and the rest are ^{12}C the statistical weighting is:

$$\frac{n!}{2!(n-2)!} = \frac{n(n-1)}{2}$$

For there to be a greater proportion of fullerenes with two ^{13}C than one ^{13}C , we therefore need:

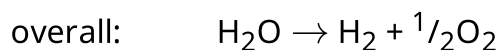
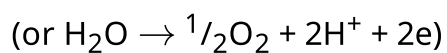
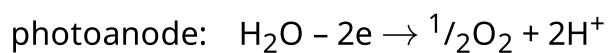
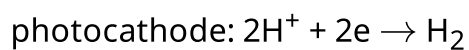
$$\begin{aligned} \frac{n(n-1)}{2} \times (0.9894)^{n-2} \times (0.0106)^2 &> n \times (0.9894)^{n-1} \times (0.0106) \\ \frac{(n-1)}{2} \times (0.0106) &> (0.9894) \\ n-1 &> \frac{2 \times (0.9894)}{(0.0106)} \\ n &> \frac{2 \times (0.9894)}{(0.0106)} + 1 \\ n &> 187.7 \\ \mathbf{n} &= \mathbf{188} \end{aligned}$$

Remember that fullerenes must have an even number of carbon atoms.

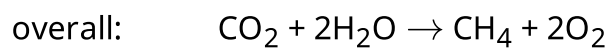
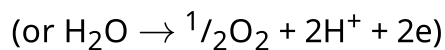
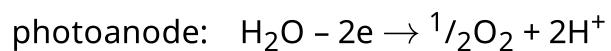
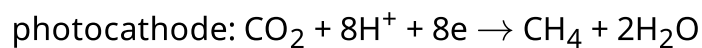


17. Photocatalysis

(a) H₂O splitting:



CO₂ methanation:



(b)

Electrochemical property	will change	will not change
Overall reaction		✓
Cathode potential	✓	
Emf		✓



(c)

i) The hole in the VB must be a stronger oxidant than oxygen, that is, lie below the level of 1.23 V and have a larger potential than 1.23 V, to be able to oxidise water to O₂. This is true for all semiconductors except Si and Cu₂O.

ii) To reduce water (H⁺ at pH 0) to hydrogen, the electron in the CB must be a stronger reductant than H₂, that is, have a more negative potential than the potential for the H⁺/H₂ redox couple (0.00 V). The edge of the CB must lie above the line E° = 0 V. This is true for all semiconductors except Fe₂O₃ and WO₃.

iii) Same as in b), but the potential must be below 0.17 V and the edge of the CB must lie above the line 0.17 V. Semiconductors: all except Fe₂O₃ and WO₃.

iv) The edge of the VB must be below 1.23 V and the edge of the CB above zero (the potential is negative). Semiconductors: TiO₂, ZnO, CdS, ZnS, and SiC.

(d) Take the interval to be 1 hour. The number of moles of incident photons:

$$n(h\nu) = \frac{E}{E_m} = \frac{Pt}{\frac{hcN_A}{\lambda}} = \frac{200 \cdot 10^{-3} \text{ J} \cdot \text{s}^{-1} \cdot 3600 \text{ s}}{\frac{(6.63 \cdot 10^{-34} \text{ J} \cdot \text{s}) \cdot (3.00 \cdot 10^8 \text{ m} \cdot \text{s}^{-1}) \cdot (6.02 \cdot 10^{23} \text{ mol}^{-1})}{532 \cdot 10^{-9} \text{ m}}} = 3.2 \cdot 10^{-3} \text{ mol}$$

The number of moles of H₂:

$$n(\text{H}_2) = 160 \cdot 10^{-6} \text{ mol} \cdot \text{h}^{-1} \text{g}^{-1} \cdot 1 \text{ h} \cdot 0.1 \text{ g} = 1.6 \cdot 10^{-5} \text{ mol}.$$

Formation of one H₂ molecule requires two electrons, hence,

$$n(e) = 1.6 \cdot 10^{-5} \text{ mol} \cdot 2 = 3.2 \cdot 10^{-5} \text{ mol}.$$

Apparent quantum yield:

$$\text{AQY} = \frac{3.2 \cdot 10^{-5} \text{ mol}}{3.2 \cdot 10^{-3} \text{ mol}} \cdot 100\% = 1\%.$$

Compared to the early photocatalytic experiments, the AQY is not bad!



18. Semiconductors

(a) CdTe consists of cadmium (Cd) and tellurium (Te), where Cd belongs to Group 12 and Te belongs to Group 16. The Cd atoms provide 5s and 5p orbitals, while the Te atoms contribute 5p orbitals. These orbitals combine to form the molecular orbitals of the crystal structure.

- The valence band of CdTe is primarily formed from the overlap of Te 5p orbitals. These are bonding orbitals, and they are filled with electrons.
- The conduction band is formed from the Cd 5s and 5p orbitals. These orbitals are higher in energy and remain unfilled in the absence of external energy (such as photons).

When light of sufficient energy (greater than the band gap) is absorbed, electrons are excited from the valence band to the conduction band, creating electron-hole pairs that are crucial for photovoltaic action.

(b) The energy of the band gap in CdTe is 1.45 eV. First, convert this energy to joules:

$$E_g = 1.45 \text{ eV} \times 1.602 \times 10^{-19} \text{ C} = 2.323 \times 10^{-19} \text{ J}$$

Then, calculate the cutoff wavelength:

$$\lambda_{cutoff} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{2.323 \times 10^{-19} \text{ J}} = 8.55 \times 10^{-7} \text{ m} = 855 \text{ nm}$$

The cutoff wavelength of CdTe is approximately 855 nm. This means that CdTe absorbs light with wavelengths shorter than 855 nm and is transparent to light with longer wavelengths.

(c) The UAE experiences intense sunlight with a peak at around 550 nm (green-yellow light). The band gap of CdTe (1.45 eV) corresponds to 855 nm, meaning it absorbs light from the UV and visible parts of the spectrum effectively, especially the shorter wavelengths where the solar intensity is strong. This makes CdTe an efficient material for capturing a significant proportion of the sunlight available in the UAE.

(d) The optical absorption coefficient at 500 nm is $2 \times 10^5 \text{ cm}^{-1}$. The penetration depth d is the inverse of the absorption coefficient:

$$d = \frac{1}{\alpha} = \frac{1}{2 \times 10^5 \text{ cm}^{-1}} = 5 \times 10^{-6} \text{ cm} = 50 \text{ nm}$$

This means that light at 500 nm penetrates only about 50 nm into the CdTe before it is absorbed.

(e) The shallow penetration depth indicates that CdTe can absorb sunlight efficiently in a very thin layer. This property is advantageous for creating thin-film solar cells, which require less material and can be manufactured at a lower cost. In the UAE, where space for large solar installations is abundant, CdTe's efficient light absorption makes it an ideal candidate for large-scale solar energy production.

(f) In bulk CdSe, the valence band is primarily formed from the Se 4p orbitals, and the conduction band is formed from the Cd 5s orbitals. The energy difference between the top of the valence



band and the bottom of the conduction band defines the band gap. In quantum dots, due to the small size of the particles, the electron and hole wavefunctions are spatially confined. This confinement increases the energy of the electronic states, effectively widening the band gap.

(g) As the size of the QD decreases, the quantum confinement effect becomes stronger, increasing the band gap. Smaller QDs absorb higher energy (shorter wavelength) photons, while larger QDs absorb lower energy (longer wavelength) photons. This tunability is advantageous in solar cells because different sized QDs can be used to capture different parts of the solar spectrum. This adaptability is particularly useful in the UAE, where sunlight is abundant across the visible and near-infrared spectrum.

(h) Using this mass approximation formula:

$$E_g(R) = E_g^\infty + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon R}$$

We can calculate the kinetic energy term first,

$$\frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = \frac{(6.626 \times 10^{-34})^2}{8(2.5 \times 10^{-9})^2} \left(\frac{1}{0.13 \times 9.109 \times 10^{-31}} + \frac{1}{0.45 \times 9.109 \times 10^{-31}} \right) \approx 0.6 \text{ eV}$$

Then, the Coulomb energy term,

$$\frac{1.8e^2}{4\pi\epsilon_0\epsilon R} = \frac{1.8 \times (1.602 \times 10^{-19})^2}{4\pi \times 8.85 \times 10^{-12} \times 10 \times 2.5 \times 10^{-9}} \approx 0.10 \text{ eV}$$

Thus, the total band gap is:

$$E_g(R) = 1.74 \text{ eV} + 0.6 \text{ eV} - 0.10 \text{ eV} = 2.24 \text{ eV}$$

(i) The bulk band gap of CdSe is 1.74 eV. For a quantum dot of 2.5 nm radius, the band gap is 2.36 eV, which is significantly higher due to quantum confinement. This shift indicates that smaller QDs absorb higher energy (shorter wavelength) light compared to bulk CdSe.

(j)

$$\lambda_{cutoff} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{2.36 \text{ eV} \times 1.602 \times 10^{-19} \text{ J}} = 555 \text{ nm}$$

(k) The absorption wavelength of 525 nm falls near the peak of the solar spectrum (~550 nm), making 2.5 nm CdSe QDs ideal for capturing solar energy in the UAE. This size of QD can efficiently absorb green light, which is a major component of the UAE's intense sunlight.

(l) The radius of the QD (2.5 nm) is smaller than the exciton Bohr radius of CdSe (5.6 nm). This indicates that the QDs are in the strong quantum confinement regime, where both the electron and hole are spatially confined, significantly altering the energy levels and increasing the band gap.



(m) In the strong confinement regime, the energy levels are quantised, leading to a larger band gap. This makes QDs highly tunable for specific optical properties. The ability to control the band gap by simply changing the size of the QDs allows for the design of solar cells that can absorb a wide range of wavelengths, improving efficiency under the UAE's sunlight.

(n) To cover the visible spectrum (400-700 nm), we can use the absorption wavelength formula:

$$\lambda_{cutoff} = \frac{hc}{E_g(R)}$$

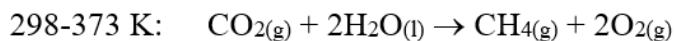
Using the bulk band gap as a lower bound ($E_g = 1.74$ eV) for 700 nm light, $R = 1.56$ nm, and using the previously calculated band gap for 555 nm light, we know that a QD radius of 2.5 nm captures this wavelength. For 400 nm light, corresponding to 7.62 eV, we need a QD radius of approximately between 1.56 nm and 7.63 nm can absorb the entire visible spectrum.

(o) Quantum dots allow for precise tuning of the solar cell's absorption profile by varying their size, making them adaptable to the wide range of wavelengths in the UAE's sunlight. Furthermore, QDs can be easily integrated into flexible and lightweight devices, which is crucial for large-scale solar installations in desert environments where efficiency, adaptability, and durability are essential.



19. Reverse combustion

(a) CO₂ methanation:

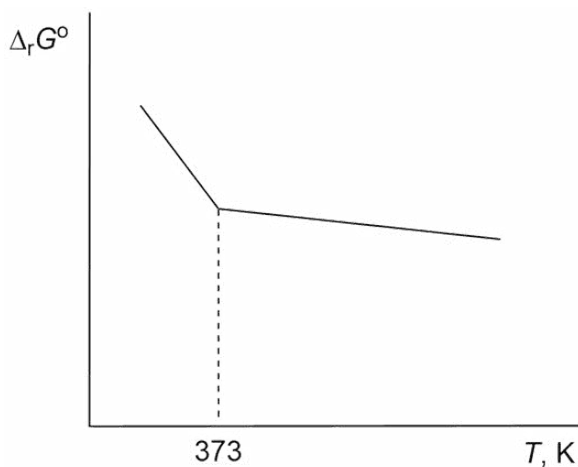


$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{890000 - 818000}{298} = 241.6 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$



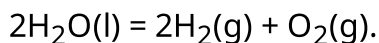
$$\Delta_r S^\circ = 241.6 - 2 \cdot 118 = 5.6 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

The graph $\Delta_r G^\circ(T)$ consists of two lines – one with a more negative slope (292-373 K), and one with a less negative slope (373-800 K).

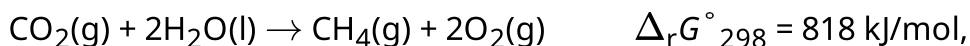


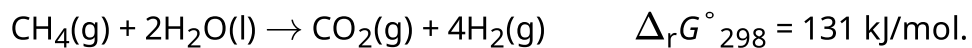
(b) The most stable system is CO₂ + 2H₂O, we take its standard Gibbs energy as zero, then $G^\circ(\text{CH}_4 + 2\text{O}_2) = 818 \text{ kJ/mol}$.

Consider decomposition of liquid water:



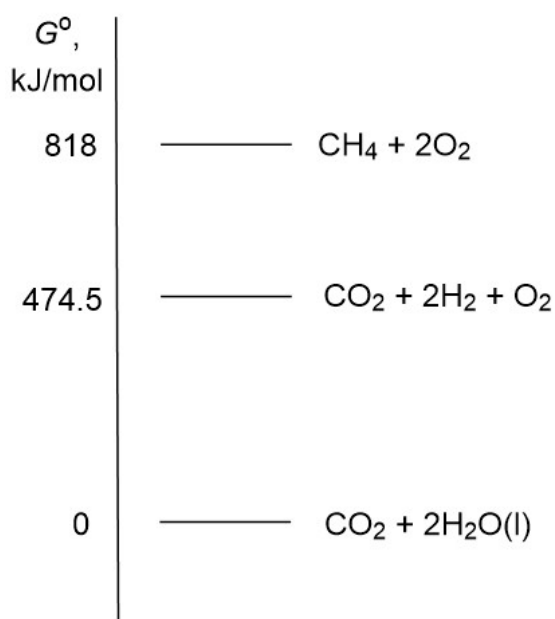
This reaction can be formally presented as a half-sum of two reactions:



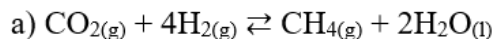


The Gibbs energy for decomposition of 2 moles of $\text{H}_2\text{O}(\text{l})$ is $(818+131) / 2 = 474.5 \text{ kJ}$, then $G^\circ(\text{CO}_2+2\text{H}_2+\text{O}_2) = 474.5 \text{ kJ/mol}$.

The Gibbs energy diagram is as follows:

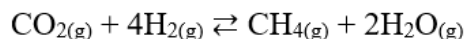


(c)



$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{-253000 - (-131000)}{298} = -409.4 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta_r H^\circ = -253 \frac{\text{kJ}}{\text{mol}}$$



$$\Delta_r S^\circ = -409.4 + 2 \cdot 118 = -173.4 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta_r H^\circ = -253 + 2 \cdot 44 = -165 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_r G_{773}^\circ = -165000 - 773 \cdot (-173.4) = -30960 \frac{\text{J}}{\text{mol}}$$

$$K_p = \exp\left(\frac{30960}{8.314 \cdot 773}\right) = 124$$

(d)

	$n(\text{CO}_2), \text{mol}$	$n(\text{H}_2), \text{mol}$	$n(\text{CH}_4), \text{mol}$	$n(\text{H}_2\text{O}), \text{mol}$
Initial mixture	1	4	0	0
Reaction	-0.9	-3.6	0.9	1.8
Equilibrium mixture	0.1	0.4	0.9	1.8

Total: 3.2 moles in the equilibrium mixture.

$$K_p = \frac{x_{\text{CH}_4} x_{\text{H}_2\text{O}}^2}{x_{\text{CO}_2} x_{\text{H}_2}^4 P^2} = \frac{\left(\frac{0.9}{3.2}\right) \left(\frac{1.8}{3.2}\right)^2}{\left(\frac{0.1}{3.2}\right) \left(\frac{0.4}{3.2}\right)^4 P^2} = 124$$

$$P = 9.7 \text{ bar.}$$



(e) Energy of one mole of photons:

$$E_m = \frac{hcN_A}{\lambda} = \frac{(6.63 \cdot 10^{-34} \text{ J} \cdot \text{s}) \cdot (3.00 \cdot 10^8 \text{ m} \cdot \text{s}^{-1}) \cdot (6.02 \cdot 10^{23} \text{ mol}^{-1})}{420 \cdot 10^{-9} \text{ m}} = 285090 \text{ J/mol}$$

The number of moles of photons:

$$n(h\nu) = \frac{n(\text{CH}_4)}{QY} = \frac{0.0011}{0.0018} = 0.61 \text{ mol}$$

Time of irradiation:

$$t = \frac{E}{P} = \frac{0.61 \text{ mol} \cdot 285090 \text{ J/mol}}{1.00 \text{ J/s}} = 173900 \text{ s} = 48 \text{ h}$$



20. New drug formulation

(a) Freezing point depression is given by:

$$\Delta T_f = K_f \cdot m$$

Where:

- $\Delta T_f = -15\text{ °C} - (-16.5\text{ °C}) = 1.5\text{ °C}$ (freezing point depression),
- $K_f = 4.5\text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$ (freezing point depression constant).

Rearrange the equation to solve for molality, m :

$$m = \frac{\Delta T_f}{K_f} = \frac{1.5}{4.5} = 0.333\text{ mol / kg}$$

So, the molality of the drug in the solution is 0.333 mol / kg.

(b) Molality, m , is defined as:

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$$

Where:

- n_{solute} is the number of moles of the drug
- m_{solvent} is the mass of the solvent in kg

Given that $m_{\text{solvent}} = 250\text{ g} = 0.250\text{ kg}$, rearrange to solve for the number of moles:

$$n_{\text{solute}} = m \cdot m_{\text{solvent}} = 0.333 \frac{\text{mol}}{\text{kg}} \cdot 0.250\text{ kg} = 0.0833\text{ mol}$$

the molecular mass of the drug:

$$M_{\text{drug}} = \frac{\text{mass of the drug}}{n_{\text{solute}}} = \frac{15\text{ g}}{0.0833\text{ mol}} = 180\text{ g/mol}$$

Thus, the molecular mass of the drug is approximately **180 g / mol**.

(c) We will use the Clausius-Clapeyron equation to estimate the new vapour pressure of the solvent after dissolving the drug.

The Clausius-Clapeyron equation is:



$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}}H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Where:

- $P_1 = 0.0075 \text{ atm}$, the vapour pressure at $T_1 = -15^\circ\text{C} = 258.15 \text{ K}$,
- P_2 is the vapour pressure of the pure solvent at T_2 ,
- $T_2 = 256.65 \text{ K}$ (-16.5°C),
- $\Delta_{\text{vap}}H^\circ = 25.0 \text{ kJ}\cdot\text{mol}^{-1} = 25000 \text{ J}\cdot\text{mol}^{-1}$,
- $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Rearrange the equation:

$$\ln\left(\frac{P_2}{0.0075}\right) = -\frac{25000}{8.314}\left(\frac{1}{256.65} - \frac{1}{258.15}\right)$$

$$\ln\left(\frac{P_2}{0.0075}\right) = -0.0681$$

$$P_2 = 0.0075 \cdot e^{-0.0681} = 0.0070 \text{ atm}$$

The vapour pressure of the pure solvent at -16.5°C is **0.0070 atm**.

With the drug dissolved, the vapour pressure decreases according to Raoult's law:

$$P_{\text{solution}} = x_{\text{solvent}} \cdot P_{\text{pure solvent at } -16.5^\circ\text{C}}$$

Calculating the mole fraction of the solvent:

$$n_{\text{solvent}} = \frac{250 \text{ g}}{100 \text{ g/mol}} = 2.5 \text{ mol}$$

Moles of the solute: $n_{\text{solute}} = 0.0833 \text{ mol}$

Then the mole fraction of the solvent is:

$$x_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{solute}}} = \frac{2.5}{2.5 + 0.0833} = 0.968$$

The vapour pressure of the solvent is:

$$P_{\text{solution}} = 0.968 \cdot 0.0070 = 0.0068 \text{ atm}$$

Thus, the vapour pressure of the solvent at -16.5°C is approximately **0.0068 atm**.



(d) The freezing point depression ensures that the drug remains in liquid form at lower temperatures, which is essential for maintaining stability during transport through colder areas in the UAE. The reduction in vapour pressure also minimises evaporation loss, which is crucial for both stability and maintaining the intended drug concentration. In high-altitude areas such as Jebel Hafeet, where temperatures can drop significantly at night, these adjustments enhance the drug's transport reliability and longevity under variable UAE climate conditions.



21. Cloud seeding

(a) If we take $h = 10$ km, the air pressure will be around 28 kPa, and we could check via the Clausius equation that the melting temperature variation is around 0.02 K from its initial value, which means that we can consider T_m as constant and that it does not depend on the pressure over this range. So, we just need to know at what height the temperature becomes 0°C .

6.5 $h = 45$, so $h = 6.92$ km, and thus at this height ice clouds can be formed.

(b) As the clouds form at 12.9 km instead of 6.92 km, the supercooling temperature is $T_{sc} = (6.92 - 12.9) \cdot 6.5 = -38.8^\circ\text{C}$.

(c) Using a Born-Haber cycle, we obtain

$$\Delta_f H^0(\text{AgI}) = \Delta_{\text{sub}} H^0(\text{Ag}) + 0.5 \Delta_{\text{sub}} H^0(\text{I}_2) + 0.5 \Delta_{\text{diss}} H^0(\text{I}_2) + \Delta_{\text{Aff}} H^0(\text{I}) + \Delta_{\text{Ion}} H^0(\text{Ag}) + \Delta_{\text{lattice}} H^0(\text{AgI})$$

$$\Delta_{f,\text{lattice}} H^0(\text{AgI}) = \Delta_f H^0(\text{AgI}) - \Delta_{\text{sub}} H^0(\text{Ag}) - 0.5 \Delta_{\text{sub}} H^0(\text{I}_2) - 0.5 \Delta_{\text{diss}} H^0(\text{I}_2) - \Delta_{\text{Aff}} H^0(\text{I}) - \Delta_{\text{Ion}} H^0(\text{Ag})$$

$$\Delta_{f,\text{lattice}} H^0(\text{AgI}) = -62 - 285 - 0.5 \cdot 57 - 0.5 \cdot 150 - (-295) - 731 = -886.5 \text{ kJ / mol}$$

(d) The numerator is the same ($16\pi\gamma_{iw}^3$) for both calculations as this parameter is determined by the water, so we can cancel it out and can directly calculate the ratio between $\Delta G_{cl}(\text{NaCl})$ and $\Delta G_{cl}(\text{AgI})$:

$$\frac{\Delta G_{cl}(\text{NaCl})}{\Delta G_{cl}(\text{AgI})} = \frac{3(\Delta G_v(\text{AgI}) + \Delta G_{sl}(\text{AgI}))^2}{3(\Delta G_v(\text{NaCl}) + \Delta G_{sl}(\text{NaCl}))^2}$$

$$\frac{108300}{\Delta G_{cl}(\text{AgI})} = \frac{3(6030 \cdot \frac{-6}{273} + 0.001 \cdot (-886500))^2}{3(6030 \cdot \frac{-10}{273} - 350)^2} = 3.19$$

$$\Delta G_{cl}(\text{AgCl}) = 33.9 \text{ kJ / mol}$$

(e) B) above the desert.

This occurs in regions where less nucleation is possible, so in the desert on a calm day. (Above the sea NaCl is the nucleation agent).

(f) The ion number on the surface is

$$N_S = \frac{4\pi R^2}{4\pi r^2} \cdot 0.8$$

The ion numbers in the particle is

$$N_V = \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi r^3} \cdot 0.7$$

where r - is ion radius and R is nanoparticle radius.

$$\frac{N_S}{N_V} = \frac{r}{R} \cdot \frac{0.8}{0.7} = \frac{0.3}{R} \cdot \frac{0.8}{0.7} = 0.00342$$

(g) From the graph we observe that the mass fraction of 75 nm nanoparticles is the same in both cases, so the mass of the second sample is also 1.08 g.

The difference between the samples is in the total surface area, as both size distributions are different.

(h) In this type of kinetics, the concentration is not the main parameter to find the order, but rather it is the total surface area which has the most influence.

Firstly, we need to distinguish different particle sizes using the mass fraction (α). Having more particles of a smaller size and mass will give a bigger surface area overall, so there is an inverse proportionality between rate and particle size.

The water does not affect the kinetics as it is in excess, so rate equation should be:

$$v = k[\text{AgI}]^n$$

where rate constant, k , is not a real constant as it depends on the particle distribution.



So k is composed of a term for each particle size.

$$k = \frac{k'}{r_1} \alpha_1^n + \frac{k'}{r_2} \alpha_2^n + \frac{k'}{r_3} \alpha_3^n + \frac{k'}{r_4} \alpha_4^n$$

We can write out the ratio of rates and could check proposed orders 0 and 1.

$$\frac{v_1}{v_2} = \frac{\frac{\alpha_{11}^n}{r_1} + \frac{\alpha_{12}^n}{r_2} + \frac{\alpha_{13}^n}{r_3} + \frac{\alpha_{14}^n}{r_4}}{\frac{\alpha_{21}^n}{r_1} + \frac{\alpha_{22}^n}{r_2} + \frac{\alpha_{23}^n}{r_3} + \frac{\alpha_{24}^n}{r_4}} \frac{k'[AgI]}{k'[AgI]} = \frac{\frac{0.2^n}{50} + \frac{0.3^n}{75} + \frac{0.4^n}{100} + \frac{0.1^n}{125}}{\frac{0.1^n}{50} + \frac{0.3^n}{75} + \frac{0.4^n}{100} + \frac{0.2^n}{125}} = 1.10$$

Analytically, this equation cannot be solved for n , but manual verification is rather simple. Order 0 is not possible, as in this case the rate would be the same in both experiments. Overall, this is a first order reaction, when we verify $n=1$, we obtain indeed 1.10 rate ratio. In this part, we don't need to think about constant units or exact total surface area of the particles, as we only need relative data comparing the two experiments. Also, how tightly packed the particles are or the surface coverage do not affect the results.



22. Kinetics of oxygen diffusion

(a) We count 16 oxygen atoms which are all inside the cell, so there are 8 SiO₂ units. Alternatively, we can count that there are 8 silicon atoms in the cell: $8 \times 0.125 + 6 \times 0.5 + 4 \times 1 = 8$, and thus are 8 SiO₂ units.

(b) If in Si we take the main diagonal, we have a Si-Si bond on both ends of diagonal. Each bond is $\frac{1}{4}$ of the diagonal. When the Si is oxidised, the oxygen atom is placed between any two silicon atoms and Si-O-Si ensemble also continues to occupy $\frac{1}{4}$ of the diagonal, so the Si-O bond is $\frac{1}{8}$ of the main diagonal.

$$8d_{\text{Si-O}} = \sqrt{3}a \Rightarrow a = \frac{8}{\sqrt{3}} \cdot d_{\text{Si-O}} = \frac{8}{\sqrt{3}} \cdot 1.54 = 7.11 \text{ \AA}$$

The ratio between unit cells is $7.11 \text{ \AA} / 5.43 \text{ \AA} = 1.31$, so the volume ratio is $1.31^3 = 2.24$

(c) We have an equilibrium between O₂ molecules in the gas phase and in the bulk/solid (where O₂ is in an atomic state or we could say a SiO₂ state). Considering the Henry's law constant, the O₂ pressure in the chamber decreases as some of the oxygen enters into the bulk. From the other side, the thickness of the layer grows (we assumed that the surface area remains constant). In any case, the volume of the wafer is negligible compared to the volume of the chamber.

$$K = \frac{[O_2]}{p_{O_2}} = \frac{\frac{n_{O_2}}{V_{Si}}}{p_0 - \frac{n_{O_2}RT}{V_{O_2}}} = \frac{\frac{l \cdot S_{\text{wafer}}}{l \cdot S_{\text{wafer}}}}{p_0 - \frac{n_{O_2}RT}{V_{O_2}}} \Rightarrow \frac{n_{O_2}}{l \cdot S_{\text{wafer}}} = K \cdot \left(p_0 - \frac{n_{O_2}RT}{V_{O_2}} \right)$$

We have two unknown values, $n(O_2)$ and the thickness, l , but the thickness depends on $n(O_2)$.

When all the Si phase is transformed to SiO₂ ($n(O_2) = n(Si)$), the thickness of the layer will be 2.24 times larger ($l = 2.24 \times l_0$) and $n(O_2) = n(Si) = 0.0167$ moles. When there is no O₂ (0.00 moles) we have ($l = l_0$).

So we could say that:

$$l = \left(1 + \frac{n_{O_2}}{0.01664} \cdot 1.24 \right) \cdot l_0$$

$$\begin{aligned} \frac{n_{O_2}}{\left(1 + \frac{n_{O_2}}{0.01664} \cdot 1.24 \right) \cdot V_{\text{wafer}}} &= 2.35 \cdot \left(1.5 - \frac{n_{O_2} \cdot 0.082 \cdot 1200}{0.5} \right) \\ n_{O_2} &= 2.35 \cdot (1.5 - 196.8 \cdot n_{O_2}) \cdot (1 + 13.88 \cdot n_{O_2}) \cdot 2 \cdot 10^{-4} \\ n_{O_2} &= 6.7 \cdot 10^{-4} \text{ moles} \\ l &= \left(1 + \frac{6.7 \cdot 10^{-4}}{0.01664} \cdot 1.24 \right) \cdot l_0 = 1.05 \cdot l_0 = 0.105 \text{ cm} \end{aligned}$$



(d) If initially there was a 1 mm wafer, if the wafer became completely oxidised its thickness would increase up to 2.24 mm (as other two dimensions do not change). From part (c), the total wafer thickness is 1.05 mm at equilibrium, therefore the oxide thickness is:

$$x = 2.24 \cdot \frac{1.05 - 1}{2.24 - 1} = 0.09 \text{ mm}$$

(e) If we consider a linearly decreasing oxygen concentration, the oxide layer will be twice as big as the previous value (i.e. 0.18 mm).

(f)

$$l_{ox}^2 + A \cdot l_{ox} = B(t + \tau) \text{ if } \tau = 0 \text{ we have } l_0^2 + A l_0 = Bt$$

We substitute the second equation in the first:

$$(l_{ox}^2 - l_0^2) + A(l_{ox} - l_0) = B$$

We obtain $A = 473.2 \text{ nm}$, $B = 94960 \text{ nm/h}$

(g) Alternatively, we could use a linear plot:

$$y = ax + b \text{ as } (l_{ox}^2 - l_0^2) = -A(l_{ox} - l_0) + B$$

Where $y = l_{ox}^2 - l_0^2$ and $x = l_{ox} - l_0$ with $-A$ value as the graph inclination and B the y value at $x=0$.

(h) Using the equation, we can solve the quadratic to determine l_{ox} .

$$\begin{aligned}(l_{ox}^2 - l_0^2) + A \cdot (l_{ox} - l_0) &= B \\ (l_{ox}^2 - 2500^2) + A \cdot (l_{ox} - 2500) &= B \\ (l_{ox}^2 - 2500^2) + 473.2 \cdot (l_{ox} - 2500) &= 94960 \\ l_{ox} &= 2517.3 \text{ nm}\end{aligned}$$

(i) Thin Oxide Limit (Initial Growth Stage): When the oxide thickness is low the linear term dominates. The equation simplifies to:

$$l_{ox} \approx \frac{B(t + \tau)}{A}$$

This represents the linear growth regime.

Thick Oxide Limit (Long Time Growth): When the oxide thickness is high the quadratic term dominates. The equation simplifies to:

$$l_{ox}^2 \approx B(t + \tau)$$



This represents the parabolic growth regime.

(j) Starting at time zero, we have the initial growth stage which is linear

$$l_{ox} = \frac{B(t+\tau)}{A} \Rightarrow l_0 = \frac{B}{A} \cdot t \text{ when } \tau = 0 \Rightarrow l_{ox} - l_0 = \frac{B}{A} \cdot \tau$$

t, min	0	5	8	12
t, h	0	1/12	2/15	1/5
l_{ox}	1000	1012.6	1019.9	1030.0
$l_{ox}-l$	0	12.6	19.9	30.0

We find $B/A = 150$, while for the previous experiment $B/A = 200$, so the temperature is not the same.

(k) B (boron): b) p.

P (phosphorus): a) n.

As (arsenic): a) n.

Ge (germanium): d) neither n nor p.

(l) For boron atoms: c)

For phosphorous atoms: b)

(m) The total thickness of the silicon and silicon dioxide layers are given as:

$$l_{Si} = 300\text{nm} = 300 \cdot 10^{-7} \text{ cm} \quad \text{and} \quad l_{SiO_2} = 100\text{nm} = 100 \cdot 10^{-7} \text{ cm}$$

Using the segregation coefficient, we have: $C_{Si} = K \cdot C_{SiO_2}$

The surface concentration of dopant is $10^{13} \text{ atoms/cm}^2$

The total amount of dopant in both layers can be expressed as:

$$C_{Si} \cdot l_{Si} + C_{SiO_2} \cdot l_{SiO_2} = N_{total}$$

$$K \cdot C_{SiO_2} \cdot l_{Si} + C_{SiO_2} \cdot l_{SiO_2} = N_{total}$$

$$\text{We obtain: } C_{SiO_2} = \frac{N_{total}}{K \cdot l_{Si} + l_{SiO_2}} = \frac{10^{13}}{0.7 \cdot 3 \cdot 10^5 + 1 \cdot 10^5}$$

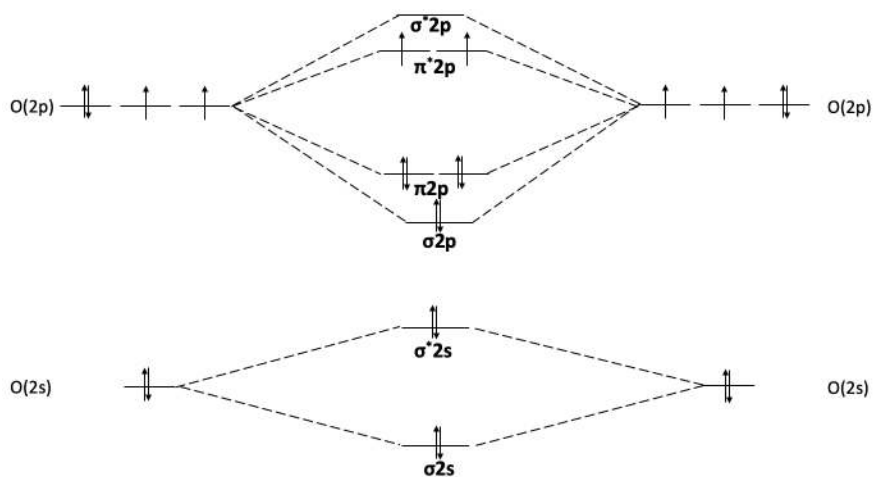
$$C_{SiO_2} = 0.322 \cdot 10^{18} \text{ atoms} \cdot \text{cm}^{-3} \text{ and } C_{Si} = K \cdot C_{SiO_2} = 0.7 \cdot 0.322 = 0.225 \cdot 10^{18} \text{ atoms} \cdot \text{cm}^{-3}$$



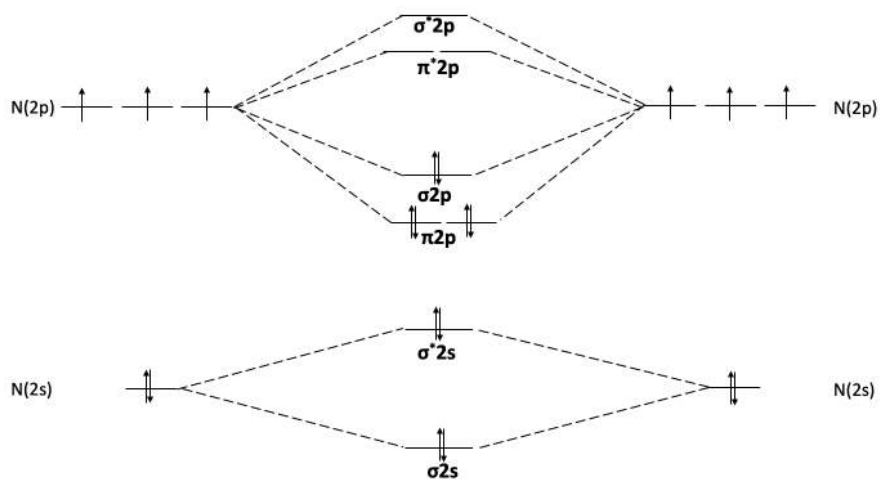
23. Molecular orbitals of diatomics

(a)

O₂:

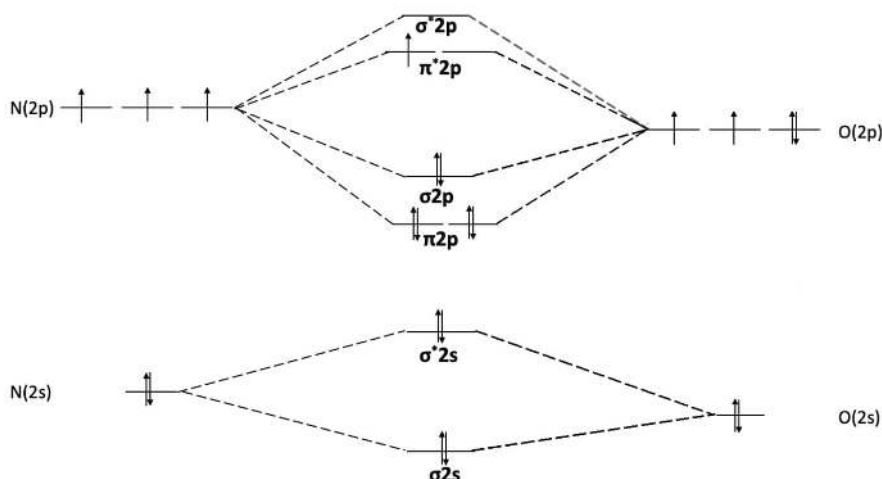


N₂:





NO:



(b) In both NO and O₂ the electron is coming from an anti-bonding orbital. Therefore the highest ionisation energy belongs to N₂, as the electron is ionised from a bonding orbital. The relative position of NO and O₂ can be deduced from the fact that nitrogen atomic orbitals have a higher energy than those of oxygen. Therefore, the order is NO: 9.26 eV, O₂: 12.07 eV, N₂: 15.5 eV.

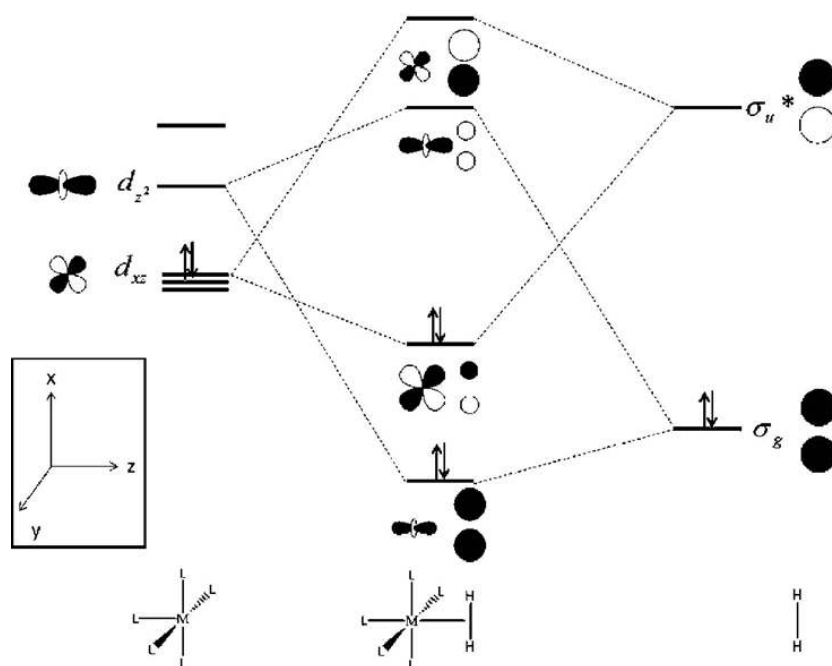
(c) Order of bond length (with bond orders given in brackets):
BaO₂ (1) > KO₂ (1.5) > O₂ (2) > [O₂][PtF₆] (2.5)

(d) In H₂O₂ the O-O moiety has partial negative charge and resembles peroxide with a single bond. In O₂F₂ there is a partial positive charge which resembles the oxygen dication with a triple bond.



24. Coordination chemistry of dihydrogen

(a)

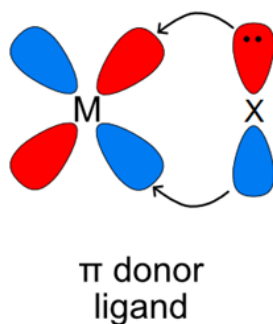


(b) $\text{W}(\text{CO})_5(\text{H}_2)$ is dihydrogen complex while $\text{Ir}(\text{PPh}_3)_2(\text{H})_2$ is a dihydrido complex. There are two reasons. Firstly, iridium(0) is a d^9 metal and therefore has more electron density occupying the anti-bonding σ^* orbital of H_2 , leading to more dihydrido character. The second reason is simply the coordination number. The tungsten complex would be six coordinate as dihydrogen and seven coordinate as dihydrido (which is high); the iridium complex would be three coordinate as dihydrogen (which is low) and four coordinate as dihydrido.

(c) $\text{W}(\text{CO})_4(\text{H}_2)(\text{PPh}_3) > \text{W}(\text{CO})_5(\text{H}_2) > \text{W}(\text{CO})_4(\text{H}_2)\text{Cl}$. The transition from a dihydrogen character to a dihydrido character results from electrons occupying the the anti-bonding orbital of H_2 . The more electron-rich the metal centre, the less dihydrogen character, and the longer the H-H distance. PPh_3 is less electron-withdrawing than CO, resulting in a more electron-rich metal. The chloride ligand has a formal negative charge, meaning that the chlorido complex is a d^5 system rather than d^6 and therefore less electron-rich.



(d)

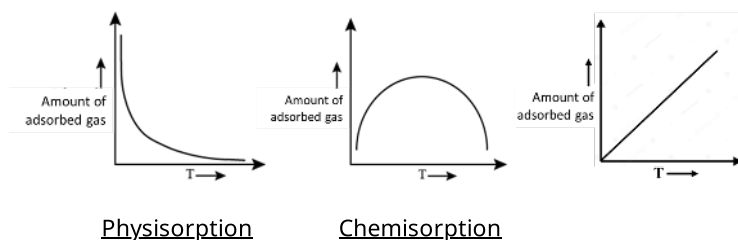


(e) $\text{Ir}(\text{CO})_3\text{I}(\text{H})_2 > \text{Ir}(\text{CO})_3\text{Cl}(\text{H})_2 > \text{Ir}(\text{CO})_3\text{F}(\text{H})_2$. The π -donating strength of halides increases with decreasing electronegativity, leading to a more electron-rich metal centre, which in turn gives the complex more dihydrido character and a higher bond length.



25. Adsorption and heterogeneous catalysis

(a)



(b) $T_1 < T_2 < T_3$

(c) (ii) ΔS is negative and ΔH should be highly negative.

(d) Al_2O_3 , SiO_2 .

(e) $0.05 \text{ L } \text{N}_2 \times \frac{1 \text{ mol}}{22.41 \text{ L}} \times \frac{6.02 \times 10^{23} \text{ molecule}}{1 \text{ mol}} \times \frac{0.16 \times 10^{-14} \text{ cm}^2}{1 \text{ molecule}} \times \frac{1 \text{ m}^2}{10^4 \text{ cm}^2} \times \frac{1}{0.5 \text{ g}} = 430 \frac{\text{m}^2}{\text{g}}$

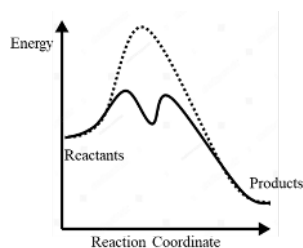
(f) (i) Nanoparticles provide higher surface areas.

(ii) Nanoparticles generally provide more active sites on the surface.

(iii) Nanoparticles allow the use of smaller amounts of expensive metal catalysts.

(g) $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$

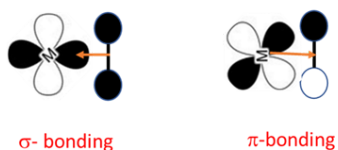
(h)



(i) Chemisorption. Since alkene hydrogenation involves H-H bond breaking, the bond should be activated which can occur only through chemisorption.

(j) σ - and π -bonding

(k)





26. Nitrogen chemistry

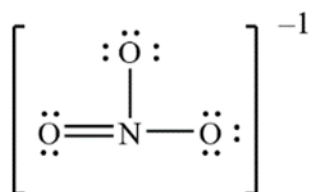
(a) From the mass percentage of iron in **D**, the molar mass of **D** can be calculated to be 227.66 g/mol, which is 65.46 g/mol higher than that of FeCl₃ and therefore the molar mass of gas **A**.

A: NOCl; **B:** NO₂; **C:** KNO₃; **D:** [NO][FeCl₄].

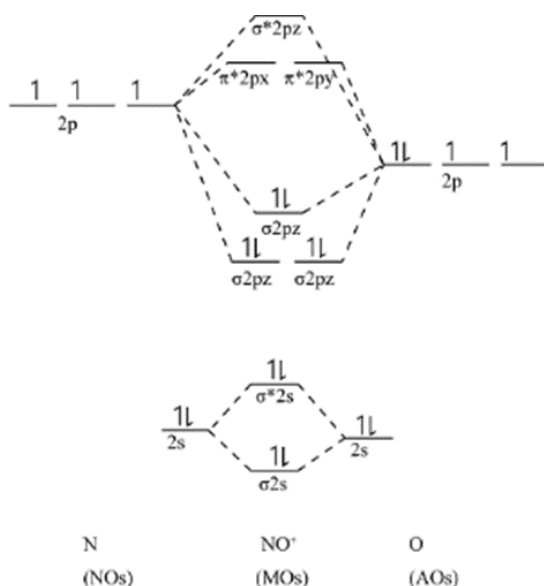
(b) **Reaction 1:** KCl + N₂O₄ → NOCl + KNO₃

Reaction 2: NOCl + FeCl₃ → [NO][FeCl₄]

(c)



(d)



(e) 117 μL/min for 3 h × 1.44 g/mL = 30.326 g N₂O₄ = 0.33 mol. The loss in mass per mol is 65.46 g per mol = 21.6 g. Total mass of reactants is 30 g (KCl) + 30.326 g N₂O₄.

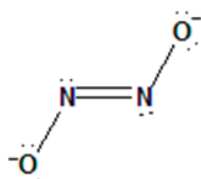


Therefore, final mass is 38.73 g.

(f) **E:** $\text{C}_5\text{H}_{11}\text{ONO}$; **F:** $\text{Na}_2[\text{ON}=\text{NO}]$; **G:** $\text{Ag}_2[\text{ON}=\text{NO}]$; **H:** AgCl ; **I:** $\text{H}_2\text{N}_2\text{O}_2$

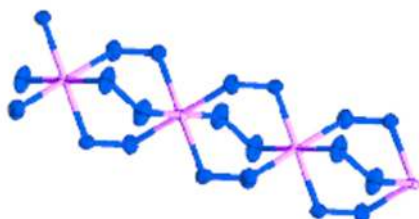
(g) $\text{C}_5\text{H}_{11}\text{ONO} + \text{NH}_2\text{OH} + 2\text{NaOEt} \rightarrow \text{C}_5\text{H}_{11}\text{OEt} + \text{H}_2\text{O} + \text{EtOH} + \text{Na}_2\text{N}_2\text{O}_2$

(h) The most stable form is the *trans* isomer.



(i) $[\text{Co}(\text{N}_2\text{H}_4)_3][\text{ClO}_4]_2$

(j)



(k) $[\text{Co}(\text{N}_2\text{H}_4)_3][\text{ClO}_4]_2 \rightarrow \text{Co} + 3\text{N}_2 + 6\text{H}_2\text{O} + \text{Cl}_2 + \text{O}_2$

(l) $58.69/353.746 \times 100\% = 16.6\%$

(m) For both cases it's the sum of all the gaseous products: 295.06 g/mol

(n) By comparing the mass loss at 1 min and 2 min we realise that the rate of mass loss is linear and constant:



	Rate (mmol/s)
Co (400 K)	0.10
Co (420 K)	0.12
Ni (400 K)	0.15
Ni (420 K)	0.17

E_a for Co: 12.7 kJ / mol for Ni: 8.7 kJ / mol

(o) The only bonds that are present in the structure of these compounds are the M-N and N-N bonds. The answer cannot be the M-N bond since that bond is stronger for Ni but the nickel compound has a lower activation energy to decompose. Therefore the answer is B) N-N bond breaking.



27. Hot desert of unknown unknowns

(a) We can start with the **A-D** cycle. We know that **A** is a binary compound and most likely an oxide because it is formed in the decomposition of **D**. From the mass fraction we can calculate that **A** is CaO. From the scheme, we guess that **D** is CaCO₃ and **U** is CO₂. So, one of the elements (**X** or **Y**) is carbon.

From the structure of polymer **M**, we can understand that **X** has a valence of three (if all bonds are single) or four (if one of the bonds is double). Similarly, **Y** and **Z** could be bivalent or trivalent. So, **X** is carbon, because only it can be 4-valent. Then one of **Y** or **Z** is bivalent and the other is trivalent.

CaO + 3C → CaC₂ + CO, so **B** is calcium carbide and **S** is CO. Without knowledge of the CaC₂ compound, it will be possible on the subsequent steps to understand that there are two carbon atoms. Compound **C** forms gas **T** and being binary **T** can contain only hydrogen as a second element. Looking through the gases where the central atom is divalent or trivalent, we do not find divalent options (e.g., H₂S is heavier than air). Of the trivalent options, NH₃ or B₂H₆ are possibilities. It is important to mention here that calcium carbide reacts with nitrogen to form calcium cyanamide CaCN₂, which upon reaction with water gives ammonia. This completes the cycle of reactions of **A-D**, and tells us that **Y** is nitrogen.

The conversion of **C** → **E** is not simple, but the main idea is that compound **E** must contain both carbon and nitrogen, and is most likely sodium cyanide, but this assumption can also be tested through identification of substance **F**. This provides further confirmation that **T** is NH₃.

Substance **F** has a molar mass of 34n g / mol according to the data on the mass fraction of oxygen:

$$M_F = \frac{16 \cdot n}{0.4705} = 34n \text{ g} \cdot \text{mol}^{-1}$$

where n is the number of oxygen atoms and n is at least 2, since this substance also contains sodium. Assuming that the molecule has two oxygen atoms, its molecular weight is 68 g / mol. Subtracting two oxygen and one sodium, we get 13 g / mol, which corresponds to CH, so **F** is sodium formate, HCOONa.



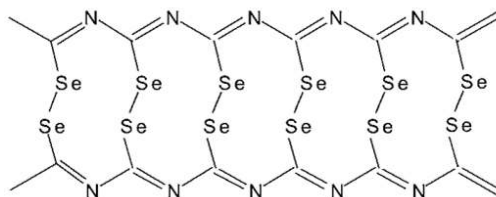
For the next step, we might assume that cyanide reacts with sulfur to form thiocyanate, but through calculations based on the data about **J** (2.02 g) and **K** (0.632 g), by subtraction we work out there is 1.388 g of **L**, and so we identify **Z** as selenium. For this we consider **J** as $(\text{ZCN})_2$ and simple disproportionation to form compounds **K** and **L** as $\text{Z}(\text{CN})_2$ and $\text{Z}_3(\text{CN})_2$:

$$\frac{0.634}{1.386} = \frac{z + 26 \cdot 2}{3z + 26 \cdot 2} \Rightarrow z = 78$$

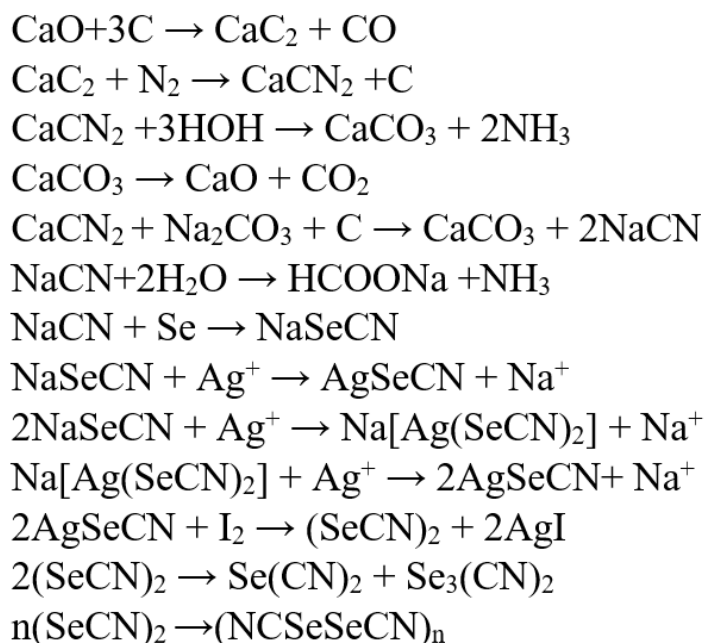
Now we have a complete list of all unknown compounds:

A CaO; **B** CaC_2 ; **C** CaCN_2 ; **D** CaCO_3 ; **E** NaCN; **F** HCOONa; **G** NaSeCN; **H** $\text{Na}[\text{Ag}(\text{SeCN})_2]$;
I AgSeCN; **J** $\text{Se}_2(\text{CN})_2$; **K** $\text{Se}(\text{CN})_2$; **L** $\text{Se}_3(\text{CN})_2$; **S** CO; **T** NH_3 ; **U** CO_2 ;

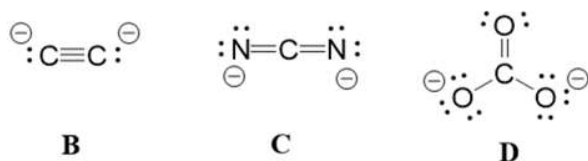
M



(b)



(c)



(d) The silver(I) cation is a soft acid, so it is more favourable for it to combine with a soft base (selenium containing anions) than with a hard base (carbon containing anions).

(e) Cyanamide

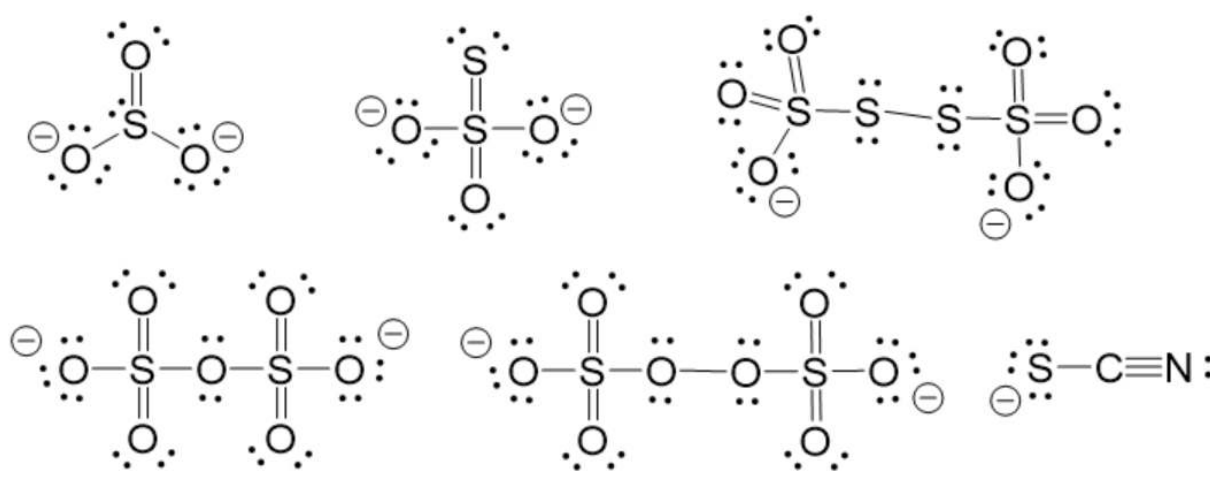


28. Analytical chemistry of the chalcogens

(a)

SO_3^{2-} (+4), $\text{S}_2\text{O}_3^{2-}$ (+2), $\text{S}_4\text{O}_6^{2-}$ (+2.5 as average or +5, 0, 0, +5), $\text{S}_2\text{O}_7^{2-}$ (+6), $\text{S}_2\text{O}_8^{2-}$ (+6), SCN^- (-2)

(b)



(c) The Henry's law constant could give the value of $\text{SO}_{2(aq)}$ or $\text{SO}_2\text{H}_2\text{O}_{(aq)}$ which is the same.

$$[\text{SO}_3^{2-}] = [\text{SO}_{2(aq)}] \cdot \frac{K_1 \cdot K_2}{[\text{H}^+]^2} \Rightarrow [\text{H}^+] = \sqrt{\frac{K_1 \cdot K_2 \cdot [\text{SO}_{2(aq)}]}{[\text{SO}_3^{2-}]}} = \sqrt{\frac{10^{-1.8} \cdot 10^{-7.2} \cdot 19.5 \cdot 10^{-9}}{10^{-6}}} = 4.41 \cdot 10^{-6} \text{ M}$$

This concentration is not dependent on solution pH, but its molar fraction is dependent.

So pH should be greater than 5.36.

The solubility of SO_2 can be then calculated considering all S forms:

$$[S^T] = [\text{SO}_{2(aq)}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] = [\text{SO}_{2(aq)}] \left(1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 \cdot K_2}{[\text{H}^+]^2} \right)$$

$$= 19.5 \cdot 10^{-9} \cdot \left(1 + \frac{10^{-1.8}}{10^{-5.36}} + \frac{10^{-1.8} \cdot 10^{-7.2}}{(10^{-5.36})^2} \right) = 7.18 \cdot 10^{-5} \text{ M}$$

(d) The quantity of the remaining forms should be 0.01% and it will be mostly the HSO_3^- form.

If we have a ratio $[\text{SO}_3^{2-}]/[\text{HSO}_3^-] = 10^4$ thus $\text{pH} = \text{p}K_2 + 4.0 = 11.2$

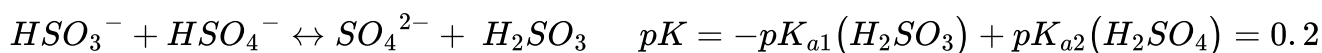


(e) The total solution volume is 200 mL and the initial concentrations of both solutions considering dilution are Na_2SO_3 (0.025 M) and NaHSO_4 (0.060 M).

First, an acid-base reaction occurs: $\text{SO}_3^{2-} + \text{HSO}_4^- \rightarrow \text{HSO}_3^- + \text{SO}_4^{2-}$

The pK of this reaction is 5.4, thus the equilibrium is completely shifted to the right giving 0.025 M of HSO_3^- and SO_4^{2-} and on the left only 0.035 M of HSO_4^- remains.

Now we should consider the remaining equilibrium which will modify slightly calculated concentrations:



$$\frac{(0.025+x)x}{(0.025-x)(0.035-x)} = 10^{-0.2} \Rightarrow x = 0.008M$$

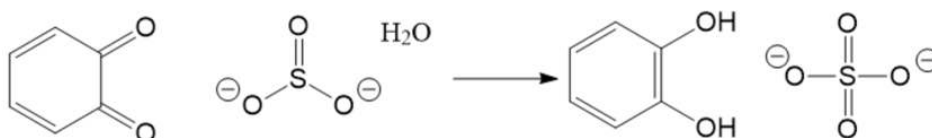
The solution pH we can calculate via the couple $\text{HSO}_4^-/\text{SO}_4^{2-}$ or via $\text{H}_2\text{SO}_3/\text{HSO}_3^-$

$$pH = pK_{a2}(\text{H}_2\text{SO}_4) + \log \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^{2-}]} = 2.0 + \log \frac{0.033}{0.027} = 2.1$$

$$pH = pK_{a1}(\text{H}_2\text{SO}_3) + \log \frac{[\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = 1.8 + \log \frac{0.017}{0.008} = 2.1$$

(f) If we write both half-reactions, we will see H^+ on the left side of the reduction process. So when pH is increasing we have less H^+ and so the equilibrium moves to the left, so the potential decreases (=redox potential is decreasing).

(g) From the standard potentials, we could find the equilibrium constant for the redox reaction:



$$\text{which is } K = \exp\left(\frac{n\Delta E^0 F}{RT}\right) = \exp\left(\frac{2 \cdot (0.69 - 0.24) \cdot 96500}{8.31 \cdot 298}\right) = 1.7 \cdot 10^{15}$$

In the first case ($c = 0.099$ M), the total reduction is not possible, as the sulfite concentration is less than the quinone concentration, so even without equilibrium calculations we can say that at least 0.001 M of quinone will remain.

For the second case ($c = 0.100$ M), both initial concentrations are the same thus:



$$K = \frac{[H_2Q][SO_4^{2-}]}{[Q][SO_3^{2-}]} = \frac{(0.1-x)^2}{x^2} = 1.7 \cdot 10^{15} \Rightarrow x = [Q] = 2.42 \cdot 10^{-9} M$$

thus the concentration is slightly bigger than the limit value. So, it is incomplete.

For the last case it is tricky to make the equation, so the easiest way is to consider that we need the concentration of quinone to be 10^{-9} M and estimate the necessary reaction quotient K' for it:

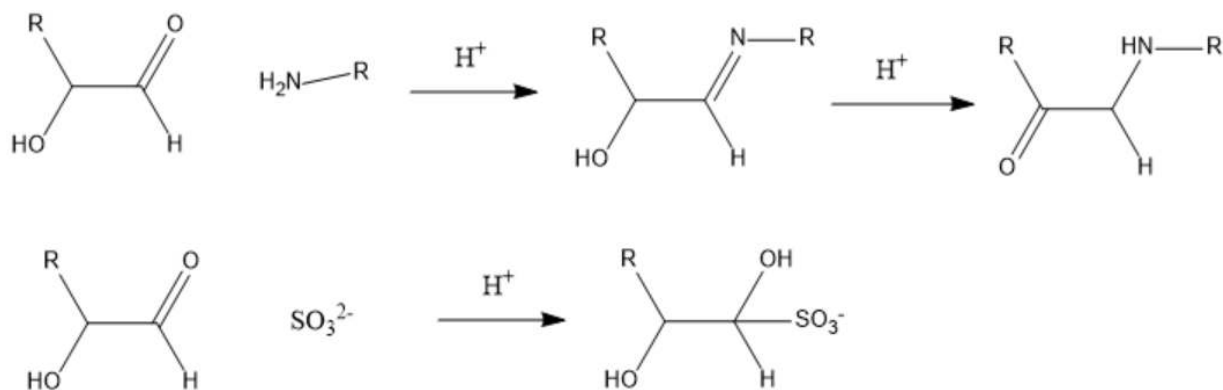
$$K' = \frac{[H_2Q][SO_4^{2-}]}{[Q][SO_3^{2-}]} = \frac{0.1 \cdot 0.1}{10^{-9} \cdot 10^{-3}} = 10^{10} < K$$

Therefore, to reach the K value, the numerator should increase and the denominator decrease, which chemically means that the quinone concentration becomes smaller and so the reaction is complete.

NB: For those who calculate the exact value of the quinone concentration you will find a value of $5.9 \cdot 10^{-15}$ M, and then you could notice that the quinone concentration in the second case is the geometric average of the first and the third cases.

(h) There is no dependence on pH.

(i)



(j)

$RNH_2 + H^+ \rightarrow RNH_3^+$ decreasing the nucleophilicity, so pH should not be too low.

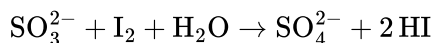
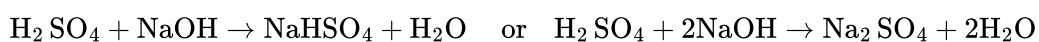
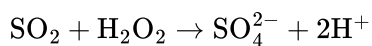
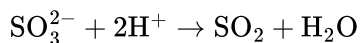
$RCH(OH)CHO + H^+ \rightarrow RCH(OH)CHOH^+$ this reaction increases the electrophilicity of the carbon atom, so pH of the solution should not be too high.

$SO_3^{2-} + 2H^+ \rightarrow SO_{2(g)} + H_2O$ sulfite ion leaves in form of SO_2 gas, so pH should not be too low.

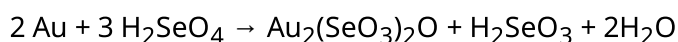
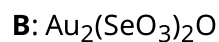
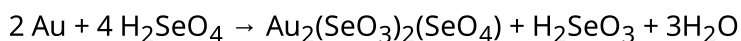
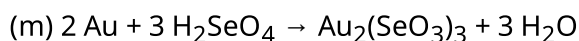
$SO_3^{2-} + 2HNO_3 \rightarrow SO_4^{2-} + 2NO_2 + H_2O$, so acid cannot be good a oxidant (or good a reductant).



(k)



(l) As selenate ion is more oxidising than a sulfate ion, so we can only state that a sulfate ion will not be reduced by a chloride ion, but we cannot conclude about bromide and iodide ions from these data.





29. Vibrational modes

(a) The number of normal modes of a linear molecule with N atoms can be calculated as $3N-5$. There are four normal modes for CO_2 : symmetric stretching, asymmetric stretching, and two bending modes.

(b) Only two bands are expected to be found in the IR spectrum of CO_2 .

- the symmetric stretching (1340 cm^{-1}) is infrared inactive.
- the asymmetric stretching shows at 2350 cm^{-1} .
- the bending modes are doubly degenerate (same energy), giving rise to only one band at 667 cm^{-1} .

(c) The number of normal modes of a non-linear molecule with N atoms can be calculated as $3N-6$. There are three normal modes for SO_2 : symmetric stretching, asymmetric stretching, and bending.

(d) The frequency of the vibration can be calculated as: $\nu = \bar{\nu} \cdot c$

For the S=O bond $\nu = 3.45 \times 10^{13}\text{ s}^{-1}$

$m_{\text{S}} = 5.32 \times 10^{-23}\text{ g}$ and $m_{\text{O}} = 2.66 \times 10^{-23}\text{ g}$

$k = 8.33 \times 10^5\text{ dyn}\cdot\text{cm}^{-1} \cong 833\text{ N}\cdot\text{m}^{-1}$

(e) The energy can be estimated as $E_{\text{osc}} = h\nu = 2.29 \times 10^{-20}\text{ J}$.

(f) For the same pair of elements, a single bond has a lower force constant than a double bond; the frequency of the stretching vibrations is lower. In the IR spectrum, the stretching bands are shifted to lower wavenumbers.

(g) The water molecule has three normal modes which results in bands at ~ 3756 , 3657 , and 1595 cm^{-1} (for free water molecules). In the solid matrix these values are slightly shifted, but can be distinguished from the sulphate anion bands, which appear in the range of approx. $1100\text{-}1200\text{ cm}^{-1}$ and around 650 cm^{-1} . The spectrum of anhydrite is c).



30. Applications of infrared spectroscopy to coordination chemistry

Part A

(a) Free NO_2^- would show three bands in the IR spectrum (symmetric stretching, asymmetric stretching, and bending). Upon coordination through the nitrogen atom, vibrations of M-NO_2 resemble those of a tetrahedral molecule, including a M-N stretching band at lower frequencies, and the rocking and wagging modes. When the coordination occurs through one oxygen atom, the N-O bonds are no longer equivalent, and each one has its own stretching frequency. This results in the appearance of an additional band in the nitrito spectrum, at 1065 cm^{-1} and the disappearance of the band at 823 cm^{-1} . Additionally, the stretching of the N-O double bond shifts to 1452 cm^{-1} .

(b) Spectrum a) nitrito isomer

Spectrum b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Spectrum c) nitro isomer

Part B

(c) As a diatomic molecule, CO has only one vibrational mode, a stretching mode, which has a wavenumber close to 2140 cm^{-1} .

Complexes of general formula $[\text{M}(\text{CO})_6]^{x+}$ have a total number of 33 vibrational modes, but only four of them are IR active (originating from a change in the dipole moment of the molecule during the vibration). These are the C-O and M-C stretching modes, and the M-C-O and C-M-C bending modes. The latter appear at wavenumbers that are lower than measured by routine laboratory FTIR spectrometers (less than 100 cm^{-1}).

(d) There are two possible geometric isomers: *cis* and *trans*.

(e) Around 2100 cm^{-1} the coordinated C-O bond stretching bands can be found. Depending on the relative position of ligands L and CO , there is going to be a modification in the dipole moment of the molecule with each vibration. The higher



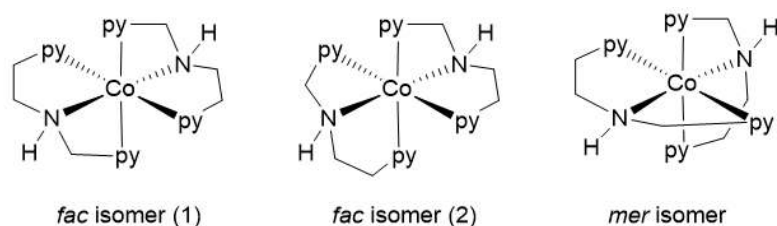
symmetry in the *trans isomer* implies that a lower number of bands would be IR active.

Part C

(f) Both pepma and bpma are tridentate ligands. Considering the L/Co^{2+} molar ratio and the fact that both **A** and **B** are mononuclear compounds, the complex species $[CoL_2]^{2+}$ should be formed. The presence of a strong band at $\sim 1100\text{ cm}^{-1}$ in the IR spectra indicates that perchlorate is present in the molecular formula of both products, as a counterion.

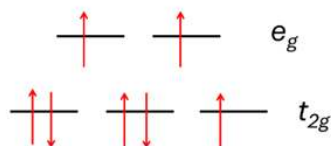
A = $[Co(pepma)_2](ClO_4)_2$ and **B** = $[Co(bpma)_2](ClO_4)_2$

The possible isomers for $[Co(pepma)_2]^{2+}$ are:



The *fac* isomer (1), where the equivalent groups are *trans* to each other is the one experimentally obtained.

(g) The experimental magnetic moment corresponds to a high-spin Co^{2+} ion in an octahedral field:



The electron configuration is: $t_{2g}^5 e_g^2$.

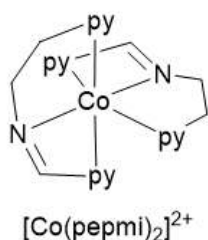
(h)

1100 cm^{-1} : Cl=O stretching from perchlorate

3292 and 3185 cm^{-1} : N-H stretching from the secondary amines



(i) In the reaction of **A** with oxygen, the metal ion remains in the same oxidation state (same magnetic moment), meaning that the oxidation occurs on the ligand. This results in a new band in the IR spectrum, which is due to the formation of a C=N double bond, since the secondary amine reacts to form an imine, as follows:



The elemental analysis of **A** and **C** are similar because their mass only differs by four hydrogen atoms.

Compound **D** is diamagnetic, which means that Co^{2+} was oxidised to Co^{3+} . Octahedral Co^{3+} complexes are typically low spin t_{2g}^6 systems. This also means there must be three perchlorate anions in **D**, which is in agreement with **B** and **D** having different elemental analysis. The formula of **D** is $[\text{Co}(\text{bpma})_2](\text{ClO}_4)_3$.



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57th ICHO - United Arab Emirates - 2025

ICHO 2025

Solutions

Practical Prep Problems



P1. Qualitative analysis of organic compounds

PART A:

1)

Vial	A1	A2	A3	A4	A5
Observations	Blue precipitate dissolves forming dark blue solution. When heated, red precipitate is formed.	Blue precipitate dissolves forming dark blue solution. No changes when heated.	Blue precipitate first dissolves and then light blue precipitate is formed.	Blue precipitate dissolves forming light blue solution.	No changes, blue precipitate turns black when heated.
Compound	Glucose	Glycine	Oxalic acid	Formic acid	Acetone



2)

Compound	Reaction(s)
Glucose	$ \begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} + \text{Cu}(\text{OH})_2 \longrightarrow \left[\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{O}-\text{Cu}-\text{O}-\text{C}-\text{H} \\ \quad \\ \text{H}-\text{C}-\text{O}-\text{Cu}-\text{O}-\text{C}-\text{H} \\ \quad \\ \text{CH}_2\text{OH} \quad \text{CH}_2\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{CHO} \end{array} \right] + 2 \text{H}_2\text{O} $ (any other reasonable structure of the complex is accepted) $ \begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} + 2 \text{Cu}(\text{OH})_2 \xrightarrow{t} \begin{array}{c} \text{COOH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} + \text{Cu}_2\text{O} \downarrow + 2 \text{H}_2\text{O} $ (the reaction can be written starting from the complex but in that case, not all coordinated glucose molecules will be oxidised)
Glycine	$ 2 \text{H}_2\text{N}-\text{CH}_2-\text{COOH} + \text{Cu}(\text{OH})_2 \longrightarrow \begin{array}{c} \text{O} \quad \text{H} \quad \text{H} \\ \parallel \quad \quad \\ \text{O}-\text{C}-\text{O}-\text{N}-\text{CH}_2-\text{C}-\text{O} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{O} \end{array} \text{ or } \begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{O}-\text{C}-\text{O}-\text{N}-\text{CH}_2-\text{C}-\text{O} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} + 2 \text{H}_2\text{O} $
Oxalic acid	$ \text{HO}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{OH} + \text{Cu}(\text{OH})_2 \longrightarrow \left(\text{Cu}^{2+} - \text{O}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{O}^- \right) \downarrow + 2 \text{H}_2\text{O} $
Formic acid	$ 2 \text{H}-\text{C}(=\text{O})-\text{OH} + \text{Cu}(\text{OH})_2 \longrightarrow \text{Cu}^{2+} + 2 \text{H}-\text{C}(=\text{O})-\text{O}^- + 2 \text{H}_2\text{O} $
Acetone	$ \text{Cu}(\text{OH})_2 \longrightarrow \text{CuO} \downarrow + \text{H}_2\text{O} $ (no reaction with acetone)



PART B:

1)

Vial	B1	B2	B3	B4	B5
Observations	Purple solution turns red and then slowly brown. When heated, brown solution is formed.	Immediate discolouration when KMnO_4 is added dropwise. When more KMnO_4 is added, the solution turns yellow.	Purple solution immediately turns green, which then slowly turns brown.	Purple solution slowly turns yellow, which slowly fades. Upon further addition of KMnO_4 the reaction proceeds faster (autocatalysis).	Dark brown precipitate is formed.
Compound	Propan-2-ol	Maleic acid	Sodium formate (+ NaOH)	Oxalic acid (+ H_2SO_4)	Phenol



2)

Compound	Reaction(s)
Propan-2-ol	$3 \text{ CH}_3\text{CH(OH)CH}_3 + 2 \text{ KMnO}_4 \longrightarrow 3 \text{ CH}_3\text{C(=O)CH}_3 + 2 \text{ MnO}_2 + 2 \text{ KOH} + 2 \text{ H}_2\text{O}$ (one of the possible reactions)
Maleic acid	$3 \text{ HOOC-CH=CH-COOH} + 2 \text{ KMnO}_4 + 4 \text{ H}_2\text{O} \longrightarrow 3 \text{ HOOC-CH(OH)-CH(OH)-COOH} + 2 \text{ MnO}_2 + 2 \text{ KOH}$ (oxidation can proceed further)
Sodium formate (+NaOH)	$\text{H-COO}^- + 2 \text{ MnO}_4^- + 3 \text{ OH}^- \longrightarrow \text{O=C-O}^- + 2 \text{ MnO}_4^{2-} + 2 \text{ H}_2\text{O}$ Further reduction of manganate is observed as green solution turns brown: $\text{H-COO}^- + \text{MnO}_4^{2-} \longrightarrow \text{O=C-O}^- + \text{MnO}_2 + \text{OH}^-$
Oxalic acid (+H ₂ SO ₄)	$5 \text{ HO-C(=O)-C(=O)-OH} + 2 \text{ KMnO}_4 + 3 \text{ H}_2\text{SO}_4 \longrightarrow 10 \text{ CO}_2 + 2 \text{ MnSO}_4 + \text{K}_2\text{SO}_4 + 8 \text{ H}_2\text{O}$
Phenol	$3 \text{ C}_6\text{H}_5\text{OH} + 4 \text{ KMnO}_4 \longrightarrow 3 \text{ C}_6\text{H}_4\text{(O)}_2 + 4 \text{ MnO}_2 + 4 \text{ KOH} + \text{H}_2\text{O}$ (the real product formed is 1:1 complex of hydroquinone and benzoquinone, called quinhydrone)



PART C:

1)

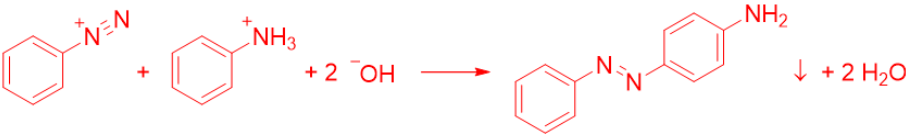
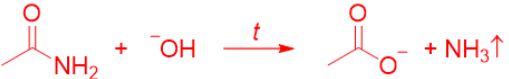
Vial	C1	C2	C3	C4	C5
Observations with H ₂ SO ₄	-	-	White precipitate is formed.	-	-
Observations with NaOH	Turbid solution, which slowly gets separated into two phases.	-	-	-	No visual changes. When heated, a distinct smell of ammonia appears.
Observations with NaNO ₂	-	Active fizzing, no colour change.	-	Yellow precipitate is formed. If acidified first with H ₂ SO ₄ and then NaNO ₂ is added, yellow solution is formed, which produces bubbles when heated and forms yellow precipitate when more of C4 and then some NaOH are added.	-
Compound	Chloral hydrate	Glycine hydrochloride	Sodium benzoate	Aniline hydrochloride	Acetamide



2)

Compound	Reaction(s)
Chloral hydrate	$\text{Cl}_3\text{C}-\text{CH}_2\text{OH} + ^-\text{OH} \longrightarrow \text{Cl}_3\text{C}-\text{H} + ^-\text{O}-\text{C}(=\text{O})\text{H} + \text{H}_2\text{O}$
Glycine hydrochloride	$\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH} + \text{NO}_2^- \longrightarrow \text{HO}-\text{CH}_2-\text{COOH} + \text{N}_2\uparrow + \text{H}_2\text{O}$
Sodium benzoate	$\text{C}_6\text{H}_5\text{COO}^- + \text{H}^+ \longrightarrow \text{C}_6\text{H}_5\text{COOH} \downarrow$
Aniline hydrochloride	If NaNO_2 is added directly to the aniline hydrochloride solution, a direct formation of the azo dye (Aniline Yellow) is observed: $2 \text{C}_6\text{H}_5\text{NH}_3^+ + 2 \text{NO}_2^- \longrightarrow \text{C}_6\text{H}_5\text{N}=\text{N}-\text{C}_6\text{H}_4\text{NH}_2 \downarrow + \text{HNO}_2 + 2 \text{H}_2\text{O}$ If first H_2SO_4 was added before adding NaNO_2, then the formation of diazonium salt is observed: $\text{C}_6\text{H}_5\text{NH}_3^+ + \text{NO}_2^- \longrightarrow \text{C}_6\text{H}_5\text{N}_2^+ + \text{H}_2\text{O}$ When heated, the diazonium salt decomposes and fizzing is observed: $\text{C}_6\text{H}_5\text{N}_2^+ + \text{H}_2\text{O} \xrightarrow{t} \text{C}_6\text{H}_5\text{OH} + \text{N}_2\uparrow + \text{H}^+$ The addition of extra aniline hydrochloride to the diazonium salt solution, followed by the addition of some NaOH leads to the formation of the azo dye (Aniline Yellow):



	 Note: The reaction between PhN_2^+ and PhNH_2 can also produce triazene Ph-N=N-NH-Ph, which should be accepted as the correct answer as well. The preference for either azo dye or triazene depends on the reaction conditions, which is not expected to be known by the participants.
Acetamide	



P2. Sørensen formol titration



$$c(\text{NaOH}) = \frac{c(\text{NH}_4^+) \cdot V(\text{NH}_4^+)}{V(\text{NaOH})} = \frac{0.1000 \cdot 5.00}{V_1}$$

The concentration of NaOH used during testing was 0.1000 M.

2) The expression to find the total amount of amino acids:

$$n(\text{AA}) = \frac{100.0 \cdot c(\text{NaOH}) \cdot V_2}{10.00 \cdot 1000}$$

3) The system of equations:

$$\begin{aligned} n(\text{AA}) &= n(\text{AA}_1) + n(\text{AA}_2) \\ m(\text{AA}) &= M(\text{AA}_1) \cdot n(\text{AA}_1) + M(\text{AA}_2) \cdot n(\text{AA}_2) \end{aligned}$$

By solving this system of equations, one finds the amount of each amino acid and can now find the mass fractions:

$$\begin{aligned} \omega(\text{AA}_1) &= \frac{M(\text{AA}_1) \cdot n(\text{AA}_1)}{m(\text{AA})} \cdot 100\% \\ \omega(\text{AA}_2) &= \frac{M(\text{AA}_2) \cdot n(\text{AA}_2)}{m(\text{AA})} \cdot 100\% \end{aligned}$$



P3. Determination of cysteine oxidation degree by two-phase titration

Step 1:

1) Appearance of red colour: $\text{Fe}^{3+} + \text{SCN}^- = \text{FeSCN}^{2+}_{(\text{aq})}$ (red)

2) The expression to find the concentration of AgNO_3 according to the Volhard titration:

$$c(\text{AgNO}_3)_1 = \frac{c(\text{KSCN}) \cdot V(\text{KSCN})}{V(\text{AgNO}_3)} = \frac{0.1000 \cdot V_1}{5.00}$$

3) Change of colour from faint green to faint pink.

Dichlorofluorescein is an adsorption indicator. Before the equivalence point, there is an excess of Cl^- ions, which are adsorbed on the surface of AgCl particles, making them negatively charged. Dichlorofluorescein is only attracted to positively charged particles, therefore, the green colour of the free indicator is observed. After the equivalence point, there is an excess of Ag^+ ions, which due to adsorption on AgCl particles, make them positively charged. These particles attract dichlorofluorescein, which due to adsorption changes colour to pink.

4) The expressions to find the concentration of AgNO_3 according to the Fajans titration and the average concentration based on two methods:

$$c(\text{AgNO}_3)_2 = \frac{c(\text{NaCl}) \cdot V(\text{NaCl})}{V(\text{AgNO}_3)} = \frac{0.1000 \cdot 5.00}{V_2}$$

$$c(\text{AgNO}_3) = \frac{c_1 + c_2}{2}$$

The concentration of AgNO_3 used during testing was 0.1000 M.



5) Without dextrin, better coagulation of precipitate is observed, and the transition becomes less sharp. Dextrin, therefore, functions as an anticoagulant. When it is used, AgCl particles are well dispersed ensuring more efficient adsorption of indicator after the equivalence point.

Step 2:

Possible dilution procedure: 10.00 cm³ in 100 cm³, then 5.00 cm³ in 100 cm³.

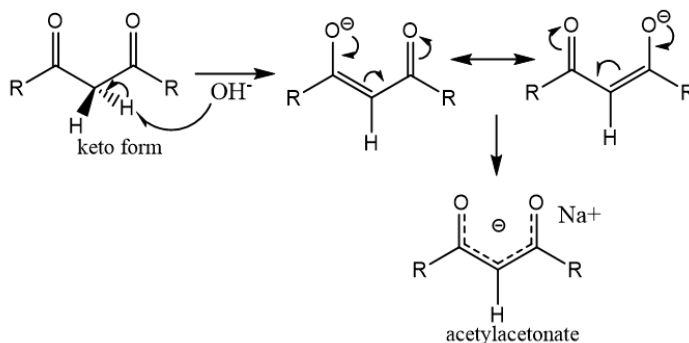
6) The expression to find the cysteine oxidation degree:

$$\begin{aligned}\text{Oxidation degree, \%} &= \left(1 - \frac{c(\text{Cys})}{c(\text{Cys})_0}\right) \cdot 100\% = \left(1 - \frac{c(\text{AgNO}_3) \cdot V_3}{V(\text{Cys}) \cdot c(\text{Cys})_0}\right) \cdot 100\% \\ &= \left(1 - \frac{c(\text{AgNO}_3) \cdot V_3}{10.00 \cdot 4.0 \cdot 10^{-4}}\right) \cdot 100\%\end{aligned}$$



P4. Synthesis and characterisation of a paramagnetic cobalt acetylacetonate complex

1.1) Mechanism of the deprotonation of β -diketone with NaOH.



1.2) Magnetic Susceptibility of the complex 'A' has been measured using a Gouy balance and the data is given in the below table (Table 1):

Compound	L(mm) Sample	weight (g) Sample	Volume Susceptibility (χ_v)	Gram Susceptibility (χ_v)	Molar mass (g/mol)	T(K)
$\text{Co}_1\text{O}_6\text{C}_{10}\text{H}_{18}$	21.00	0.0879	0.106×10^{-4}	0.346×10^{-4}	293.2	298

1.3)

a) Molar susceptibility of this complex χ_m :

Molar mass of complex A = 293.18 g/mol

Gram susceptibility obtained from the Gouy balance: 0.346×10^{-4} cc/g

Molar susceptibility (χ_M) = $\chi_g \times \text{molar mass}$



$$= 0.346 \times 10^{-4} \text{ cc/g} \times 293.18 \text{ g/mol}$$

$$= 0.010144 \text{ cc/mol}$$

b) Spin only Effective magnetic moment (μ_{eff}) in BM (Bohr's magnetons) of the complex can be determined using the following formula.

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_M \times T}$$

$$\mu_{\text{eff}} = 2.828 \sqrt{0.010144 \times 298}$$

$$\mu_{\text{eff}} = \underline{\underline{4.91 \text{ BM}}}$$

c) Number of unpaired electrons

Number of unpaired electrons in compound A: 3

$$\mu_{\text{eff}}(\text{spin only}) = \sqrt{n(n+2)} \quad \text{here } n = \text{number of unpaired electrons}$$

The observed μ_{eff} value (4.91 BM) corresponds to 3 unpaired electrons at the metal center

Oxidation State of the Co center is therefore: +2

Note: the effective magnetic moment observed for the compound A (4.91 BM) is greater than the magnetic moment calculated from the spin only formula. This indicates that in addition to the spin angular momentum, the moment arising from the orbital motion of the electrons also contributes to the observed magnetic moment. For first row transition metals ions, the orbital contribution to the magnetic moment usually arises from a partially filled t_{2g} (d_{xy}, d_{yz}, d_{xz}) orbital configuration.

2.2) Using a Gouy or faraday balance, record the magnetic susceptibility of the complex B

Magnetic Susceptibility of the compound 'B' has been investigated using a Gouy balance

Complex B behaves like a diamagnetic material

Volume magnetic susceptibility χ_v observed is zero

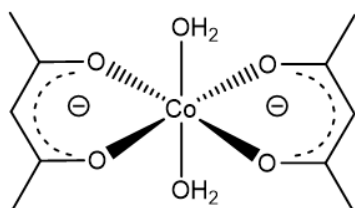


3.1) Concentration of the Cobalt in Solution A can be determined using the Beer-Lambert Law: $A = \epsilon c l$

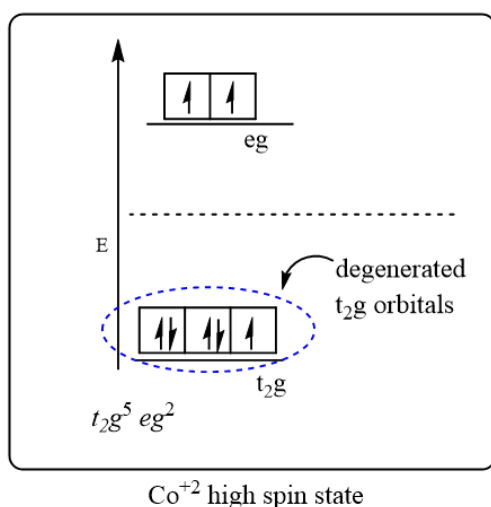
Concentration $c = A/\epsilon l$ here $\epsilon = 1.45 \times 10^4 \text{ cm}^{-1} \cdot \text{l} \cdot \text{mole}^{-1}$, $l = 1 \text{ cm}$ $A =$
absorbance measured at 500 nm

3.2) Using the magnetic data, provide the following information for the complex A

- Ground Spin state: $3/2$ (high spin)
- Oxidation state of the Co center: Co^{+2}
- Most probable geometry: Octahedral geometry
- Draw the structure of the complex



- Draw the possible d orbital splitting for this complex with electronic distribution

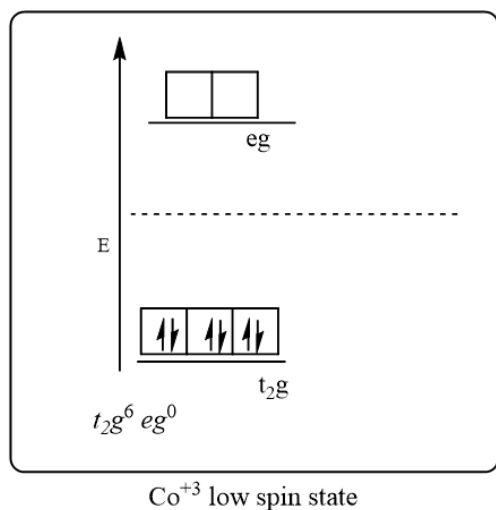


3.3) Using the magnetic data, provide the following information for the complex B

- Ground Spin state: zero



- Oxidation state of the 'Co' center: Co^{+3}
- Most probable geometry: Octahedral geometry
- Draw the possible d orbital splitting for this complex with electronic distribution



3.4) From your observation, how does the oxidation at the metal center affect the magnetic behavior and spin state of the complex A?

Oxidation at the cobalt center drastically changes the magnetic behavior.

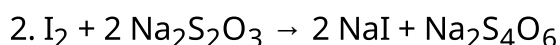
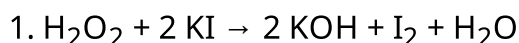
Compound A with Co^{+2} is paramagnetic with a high spin electronic configuration.

Compound B with Co^{+3} is diamagnetic with a low spin electronic configuration.



P5. Never late with thiosulfate

(a)



(b) As we see from the reaction, the neutralisation of the base OH^- by H^+ will shift the equilibrium toward the products with increasing H^+ concentration.

(c) Dextran, Amylose

(d) The linear dependence should be observed - so the order is 1.

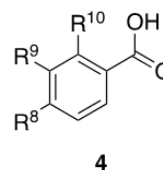
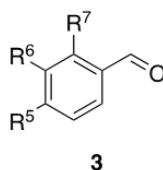
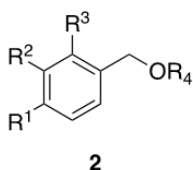
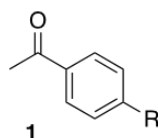
(e) The second clock will not have the instant colour change because the solution is not homogeneous, we should to continue to work with tubes.

(f) The colour should change in two "chemical minutes" showing that decrease in concentration two times leads to a decrease in reaction rate of two times, therefore 1st order kinetics.

(g) In this case the solution of H_2O_2 which has been 2 or 3 times diluted, it should show 4 or 6 "chemical minutes".

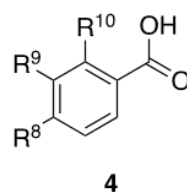
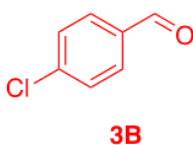
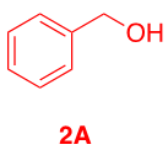
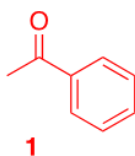


P6. To condense or not to condense?



For the test of the task the following red chemicals were used. The chemicals 2 and 3 were dissolved in EtOH (3 mL) and the solutions were tested.

If any substitution of the chemicals is made, it is recommended to test the alternatives (for instance, *p*-anisaldehyde can be used instead of *p*-Cl-benzaldehyde). After the appropriate chemicals are chosen, it is recommended to insert appropriate GHS codes of the chemicals in the table at the end of the test paper.



Part A: Condensation reaction with compounds A and B

Reaction between 1 and 3B.



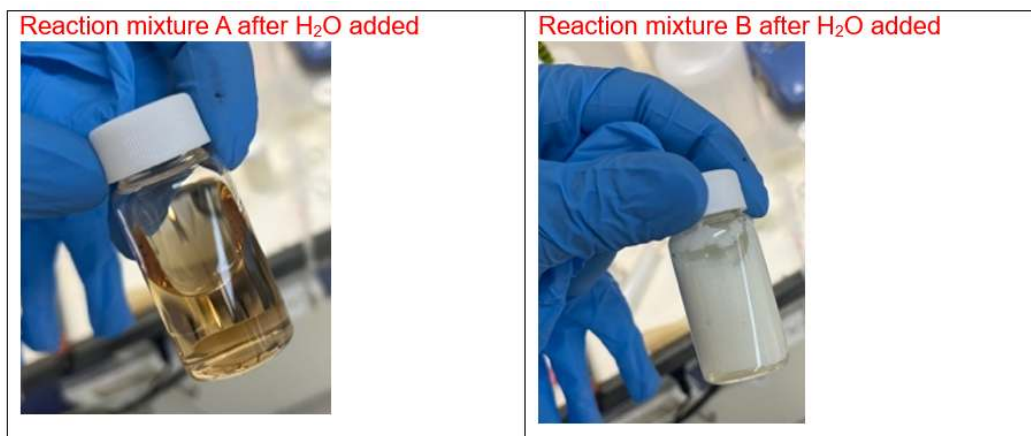
Q1: Choose the appropriate answer about the observations below (reaction mixture 1+2A).

Is it possible to distinguish reaction completeness by this TLC?	Yes/ No
Is it better to use another eluent mixture?	Yes /No
Is reaction completed?	Yes/No/ Unknown
Is there a product formation observed by TLC?	Yes/No/ Unknown
Is there any visible sign of the reaction (gas evolution or precipitate formation)?	Yes/ No

Q2: Choose the appropriate answer about the observations below (reaction mixture 1+3B).



Is it possible to distinguish reaction completeness by this TLC?	Yes/ No
Is it better to use another eluent mixture?	Yes /No
Is reaction completed?	Yes/No/ Unknown
Is there a product formation observed by TLC?	Yes/No/ Unknown
Is there any visible sign of the reaction (gas evolution or precipitate formation)?	Yes /No (Precipitate was formed in the reaction)



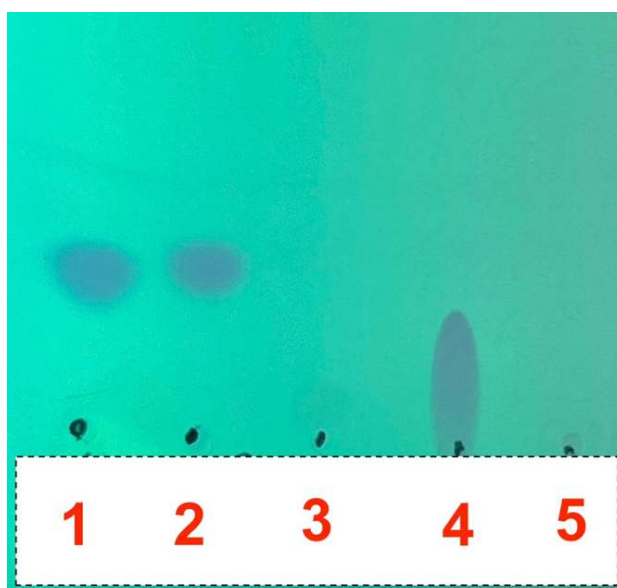
Q3: According to the observations, choose the correct structures for compounds **A** and **B** in the table below.

2: A	3: B	4: -
-------------	-------------	------

Q4: Which property/properties of compounds 2-4 allowed you to differentiate between them? Choose all that applies.

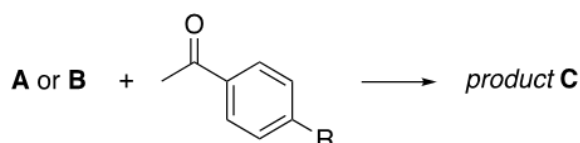


- A. Magnetic properties.
- B. Red-Ox properties.
- C. Acid-base properties.
- D. Electrochemical properties.
- E. Photophysical properties. (compound 2A poorly absorbs UV-light)



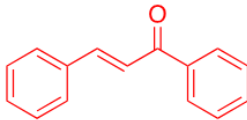
On the picture above, TLC of compounds **1-4** is presented. Additionally, lane 5 demonstrates TLC of compound **4** (PhCO₂H) in the same reaction mixture described in the task but with compound **4** (sodium salt of acid is formed which is poorly soluble in EtOAc, thus, almost invisible spot stays at the starting line).

Part B: product analysis





Q5: Answer the questions below and draw the structure of product C. Assume that all the substituents (R and R_n) are hydrogens for the product structure.

Was there a gas evolution?	Yes/ No
Was there a precipitate formation?	Yes /No
Was there a colour change?	Yes /No
Is it possible to detect this chemical on TLC by permanganate stain visualization instead of UV visualization?	Yes /No
Structure of C	

Part C: more condensations?



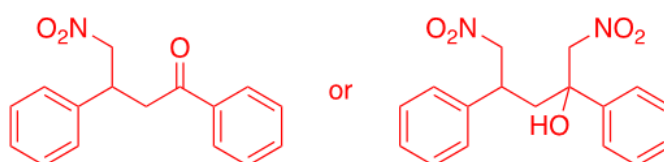
1 - reaction mixture concentrated

2 - reaction mixture diluted

3 - product C

Nitromethane is invisible on TLC plate under UV visualization.

Q6: Draw a possible structure of product D that can be formed in the reaction performed. Assume that all the substituents (R and R^n) are hydrogens for the product structure.



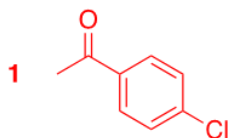
Q7: Choose the appropriate answer about the observations below.



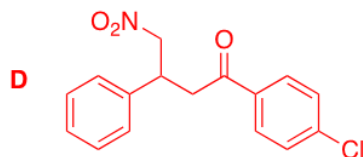
Is it possible to distinguish reaction completeness by this TLC?	Yes/No
Is it better to use another eluent mixture?	Yes/No
Is reaction completed?	Yes/No/Unknown
Is there a product D formation observed by TLC?	Yes/No/Unknown

Part D: what are the products?

Q8: Draw the structures of compounds **1** and **D** that fit the presented spectra.



Chemical Formula: C_8H_7ClO
Molecular Weight: 154.5930

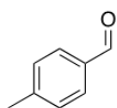


Chemical Formula: $C_{16}H_{14}ClNO_3$
Molecular Weight: 303.7420

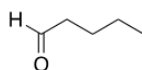


P7. Breakfast of carbonyls

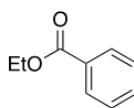
The list of chemicals tested:



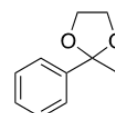
1
B-1



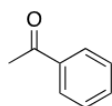
3
E-3



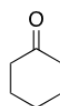
5
C-5



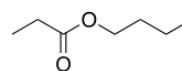
7
G-7



2
A-2



4
D-4



6
F-6

There are many alternatives, that can be used instead of the tested chemicals. Below, one might find a list of alternative chemicals suggested. However, **we recommend to test the alternatives** beforehand to confirm a chemical substitution. According to the chemical chosen, we recommend filling in the table with GHS hazard codes in the question text.

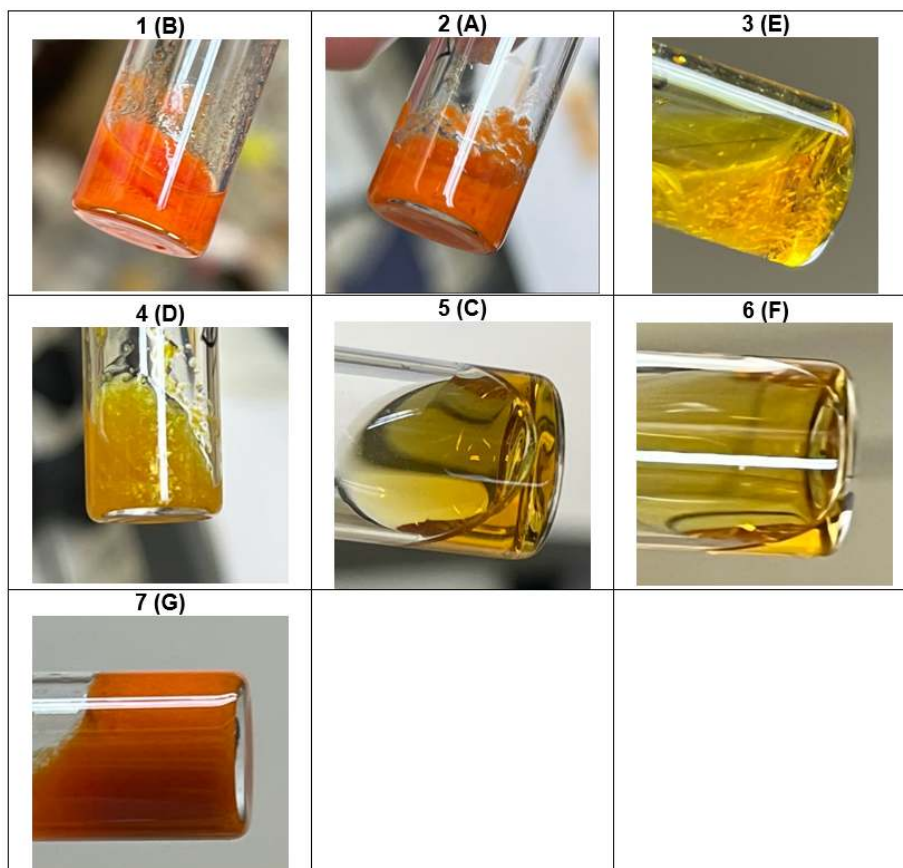


Chemical	Alternative(s)
 1	 vanillin
 3	 citronellal
 4	
 6	

Part B: Analysis of unknowns

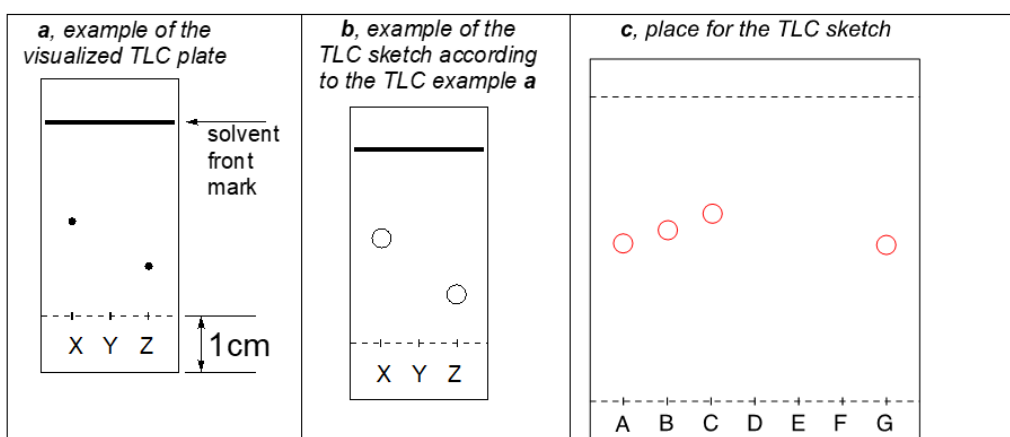
Q1: Note the observations in the table below.

Sample	A	B	C	D	E	F	G
Observation							
P – precipitate	P	P	N	P	P	N	P
N – no precipitate							



Q2: Sketch the TLC plate according to the example shown below.

The sketch of the TLC must be compared to the TLC observed as it may depend on the TLC plates and chemicals used.



Q3: Note the observations in the table below.



Sample	A	B	C	D	E	F	G
Observation							
V – visible	V	V	V	N	N	N	V
N – not visible							

Q4: Write the observations in the table below. Note: A clear reaction should be observed. Repeat the experiment for the vials where the result is not clear enough.

Sample	A	B	C	D	E	F	G
Observation							
P – positive Tollens test	N	P	N	N	P	N	N
N – negative Tollens test							



Only in vials 1 and 3 the silver mirror is observed.

The overheating of the reaction mixture may lead to inferior results (below reaction with chemical 1 was performed three times; below, compare trials 1 and 2 to



overheated trial 3). A weak silver mirror can be observed in case of 3, however, it is recommended to repeat the reaction to avoid errors.



Other compounds may give artefacts (small amount of grey precipitate, but not a mirror!) if overheated or/and not sufficiently pure. Therefore, we recommend to test the chemicals before the exam is given to students.

For the standard preparation of Tollens reagent refer to this source:

<https://edu.rsc.org/experiments/the-silver-mirror-test-with-tollens-reagent/822.article>

Q5: Suggest the structure of unknown chemicals below. If some chemicals cannot be differentiated after the tests performed, write down all the possible numbers that can be assigned to chemicals.

Sample	A	B	C	D	E	F	G
Unknown	27	1	5	4	3	6	27

Q6: From the list below choose appropriate reagent(s) that can be used to figure out the remaining chemicals if any.

a) NaOH

b) NaOH, I₂

c) EtOH



d) $\text{Na}_2\text{S}_2\text{O}_3$, EtOH

e) $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$, EtOH

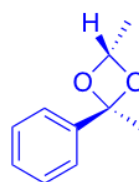
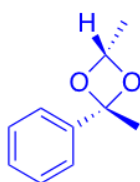
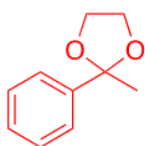
f) NaBH_4 , EtOH

Q7: Analyse the mass-spectra of the compounds **5** and **7** below and suggest possible structure(s) for them.

PhCO_2Et is the only reasonable option for compound **5**.

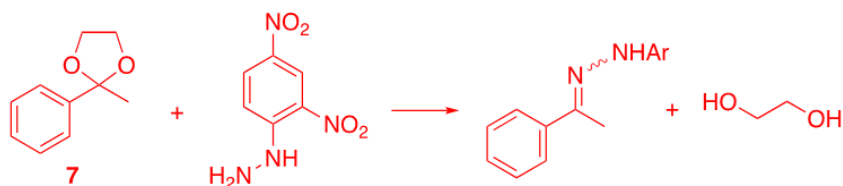
Dioxolane is the most probable option for **7** (red molecule), while dioxetanes are quite unstable (blue molecules).

Chemical Formula:
 $\text{C}_{10}\text{H}_{12}\text{O}_2$



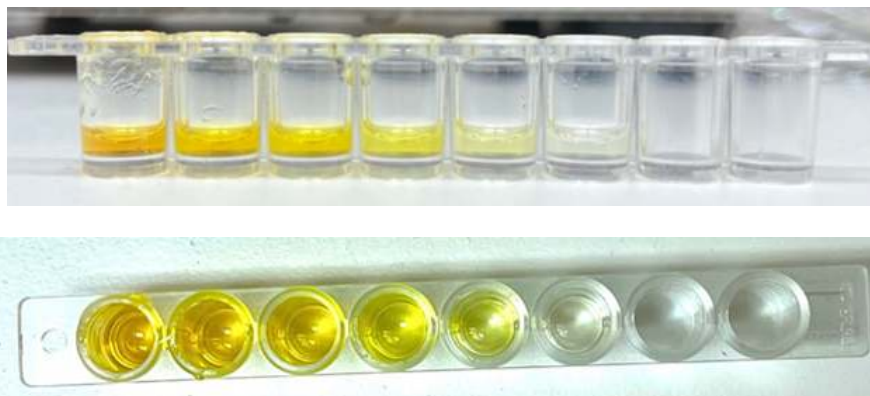
Q8.

$5 + \text{DNPH} = \text{no reaction}$



Part C: Analysis of DNPH concentration

Q9: Compare the concentration of the unknown DNPH sample with the concentration of the prepared DNPH solution, e.g. $5 \times c(\text{prepared}) < c(\text{unknown}) < 7 \times c(\text{prepared})$.



It is recommended to perform this test and choose the most suitable concentration according to the biggest difference seen with the eye (in the test performed, the best concentration range was approximately $c(\text{prepared}) = 150 \times c(\text{unknown})$).



References and credits

Q2. (i) Faraday, M. **On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat** *Phil. Trans. R. Soc.*, 1825, 115, 440-466. (ii) Willett, K. L. *et al.* **Differential Toxicity and Environmental Fates of Hexachlorocyclohexane Isomers** *Environ. Sci. Technol.*, 1998, 32, 2197-2207. (iii) Dong, X. *et al.* **Merging shuttle reactions and paired electrolysis for reversible vicinal dihalogenations** *Science*, 2021, 371, 507-514. (iv) Law, R. J. *et al.* **Hexabromocyclododecane Challenges Scientists and Regulators** *Environ. Sci. Technol.*, 2005, 39, 281A-287A. (v) Bescós, A. *et al.* **Theoretical insight on the treatment of β -hexachlorocyclohexane waste through alkaline dehydrochlorination** *Sci. Rep.*, 2021, 11, 8777. (vi) Vijgen, J. **The Legacy of Lindane HCH Isomer Production Main Report A Global Overview of Residue Management, Formulation and Disposal International HCH & Pesticides Association** *International HCH & Pesticides Association*, 2006.

Q14, Q15. Mass spectra: NIST Standard Reference Database 69: NIST Chemistry WebBook, <https://webbook.nist.gov/>

Q16. The images of Goldberg polyhedra are taken from the work of the author Tomrueen on Wikipedia. (i) Goldberg, M, **A Class of Multi-Symmetric Polyhedra** *Tohoku Mathematical Journal, First Series*, 1937, 43, 104-108. (ii) Kroto, H., Heath, J., O'Brien, S. *et al.* **C₆₀: Buckminsterfullerene** *Nature* 1985, 318, 162-163.

Q29. The infrared spectra of calcium sulphates are taken from Stuart, B. **Infrared spectroscopy: fundamentals and applications**, John Wiley & Sons Ltd, 2004.

Q30. Anjana S. *et al.* **Controlling oxidation of bis-tridentate cobalt(II) complexes having bis(2-pyridylalkyl)amines: Ligand vs. metal oxidation** *Dalton Trans.*, 2017, 46, 10830-10836.

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