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

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

area of triangle	$A = \frac{1}{2}ab \cdot sinC$
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	$\mathrm{E} = \frac{hc}{\lambda}$
Beer-Lambert law	$A = \log\frac{I_0}{I} = \varepsilon cl$
spin only magnetic moment	$\mu = \sqrt{n(n+2)}\,\mathrm{BM}$
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$
0^{th} order integrated rate law	$[\mathrm{A}] = [\mathrm{A}]_0 - kt$
1^{st} order integrated rate law	$\ln[\mathrm{A}] = \ln\,[\mathrm{A}]_0 - kt$
Arrhenius equation	$k = A \cdot e^{-\frac{E_a}{RT}}$
enthalpy	$H = U + pV$
Gibbs energy	$G = H - TS$
standard Gibbs energy change	$\Delta_r G^\mathrm{o} = -RT\ln K = -nFE^o_{cell}$
Clausius-Clapeyron equation	$\ln\frac{P_1}{P_2} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
Raoult’s law	$p_i = x_i p_i^*$
boiling point elevation	$\Delta T = iK_b m$
freezing point depression	$\Delta T = iK_f m$

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 ($R\text{-}NO_2$)	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
cis-$M(CO)_4X_2$	4
trans-$M(CO)_4X_2$	1
fac-$M(CO)_3X_3$	2
mer-$M(CO)_3X_3$	3
fac-$M(CO)_3X_2Y$	3
cis-$M(CO)_2X_4$	2
trans-$M(CO)_2X_4$	1

Periodic table

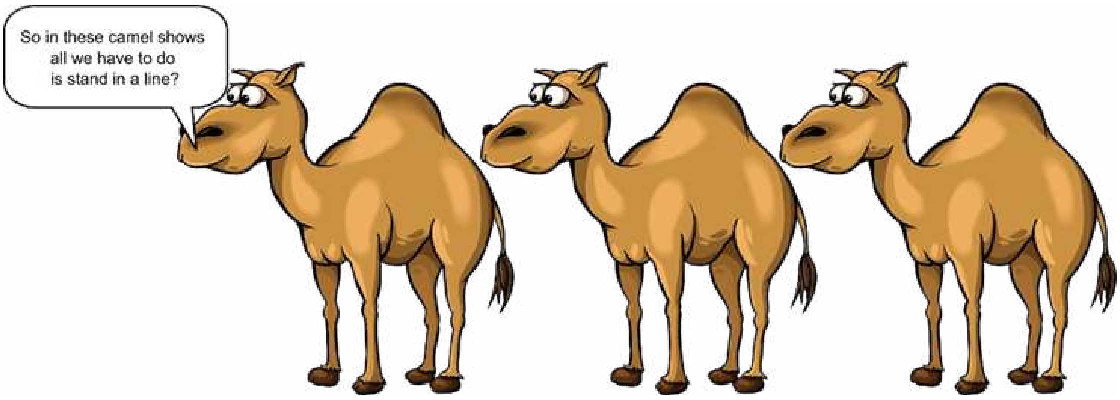
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	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

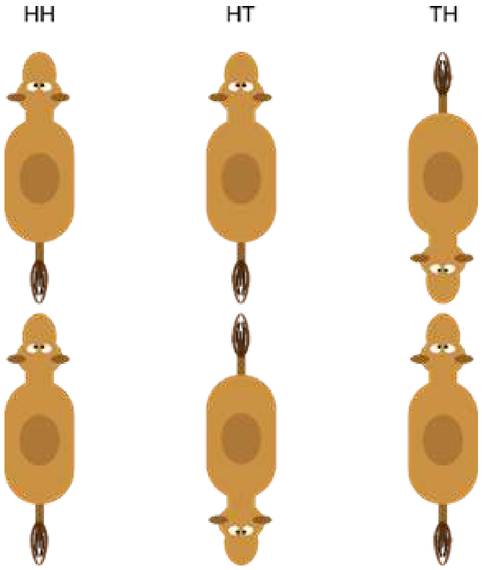
A nighttime camel show in the UAE

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.

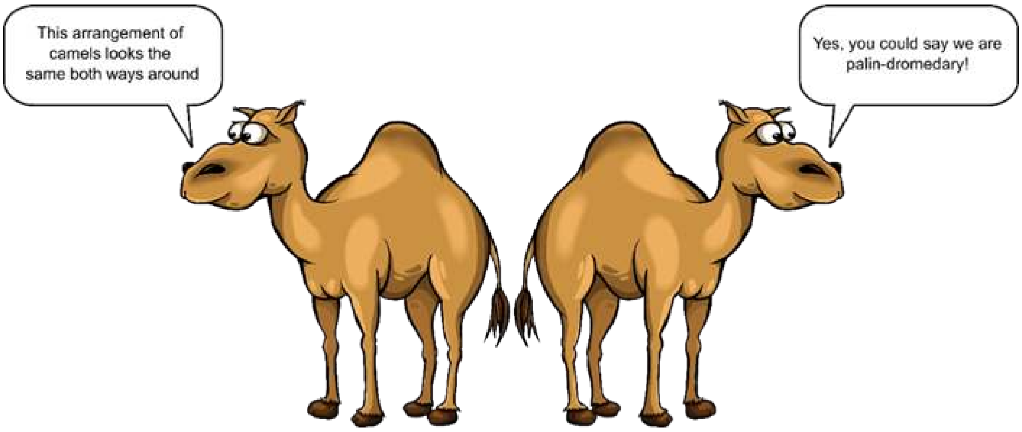


The three arrangements possible when viewed from overhead are shown above. We could call these three arrangements HH, HT, and TH respectively, based on whether the head or the tail of the camel comes first as we look from top to bottom. We might at first think that there is a fourth possible arrangement 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.

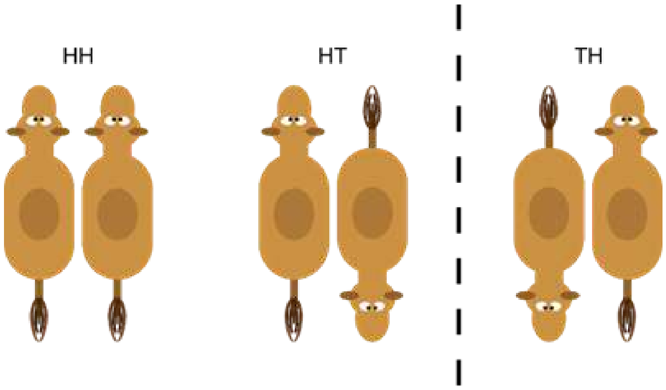
This question requires you to draw various arrangements of camels. If your artistic skills have deserted you somewhat, then you may approximate a camel to something simpler in your drawings such as an arrow. It is important to remember though that camels are three dimensional objects.

(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.

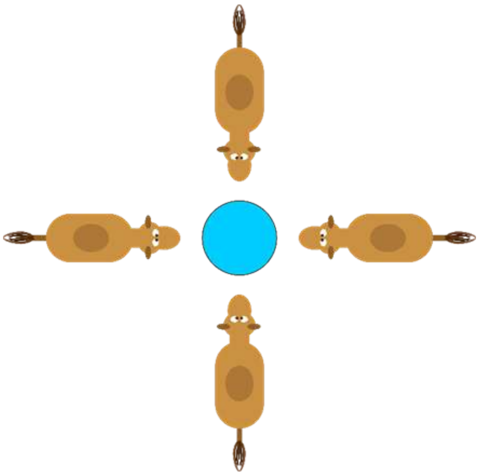


When viewed from overhead, and described going left to right, we can call these arrangements HH, HT, and TH respectively. Again, we might think there is a fourth possible arrangement of camels (TT), but this is the same as HH if viewed from the other side. The HT and TH arrangements are also interesting, 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.

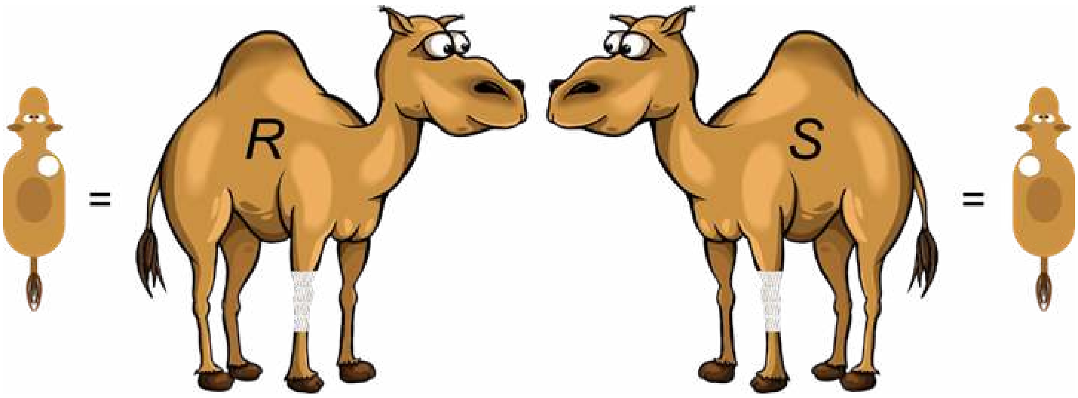
Although camels are famous for going for long periods without water, they do sometimes need to drink. A particular well has space for four camels to stand around it and drink water. To do this, the camels should be arranged around the well as shown.



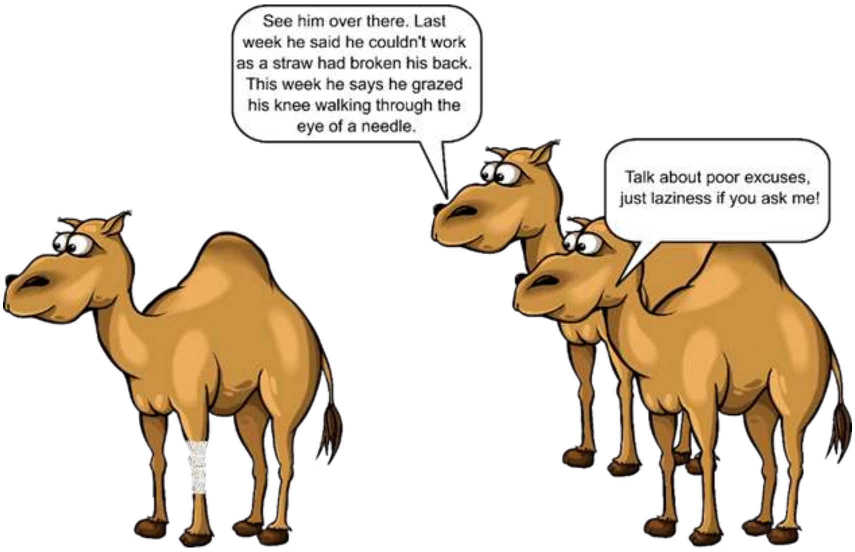
However, Colin was forgetful again and did not pay attention to which was the head end, and which was the tail end, when tying them up.

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

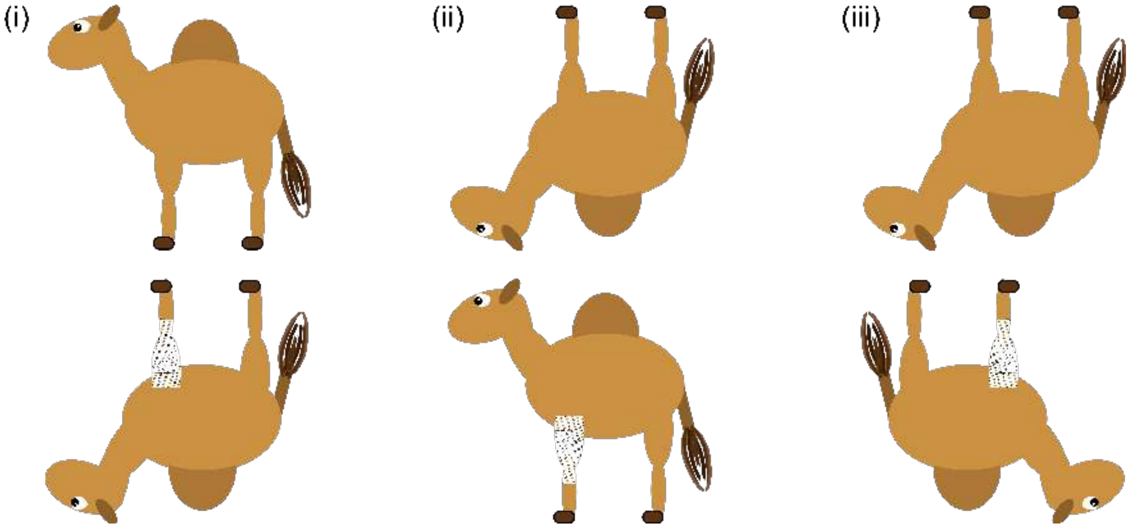
Carrying people across the desert is an arduous task for camels. Camels bend their front legs to sit down when carrying a rider and sometimes this leads to them injuring a leg. An individual camel who has injured one leg is no longer achiral and becomes a chiral camel. We will call chiral camels who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

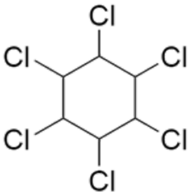
No camels were harmed in the making of this question.

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

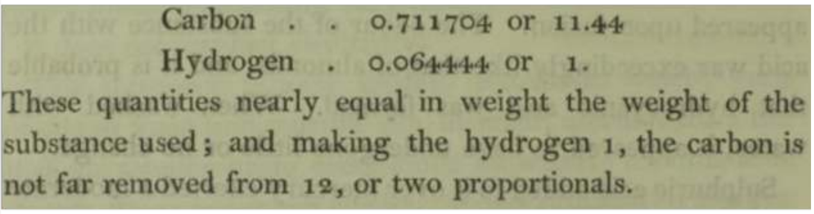
In the fairy tale *Snow White*, the evil queen looks at her reflection in the mirror and asks, "*Mirror mirror on the wall, who is the fairest one of all?*" The queen assumes she sees her exact self in the mirror; however, this is not always true. The reflection of a chiral object in a mirror gives its 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.

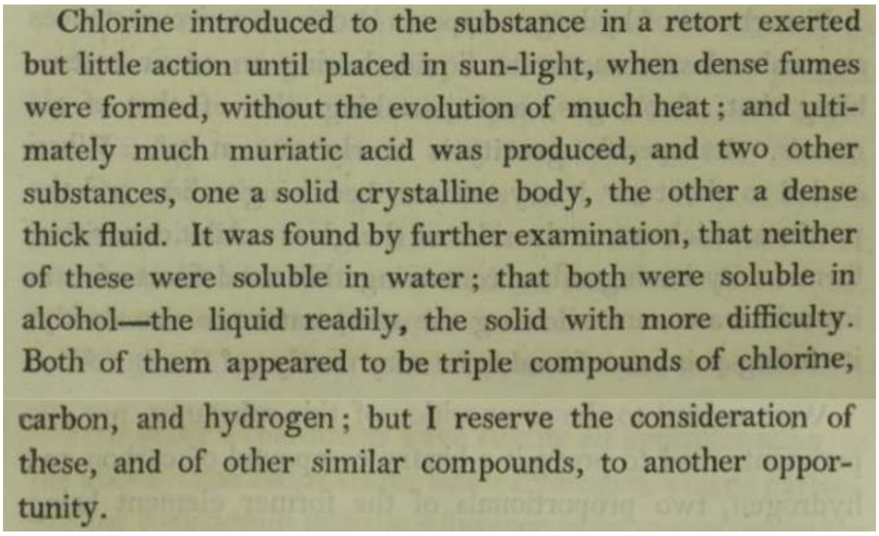


Carbon . . 0.711704 or 11.44
Hydrogen . 0.064444 or 1.

These quantities nearly equal in weight the weight of the substance used; and making the hydrogen 1, the carbon is not far removed from 12, or two proportionals.

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.

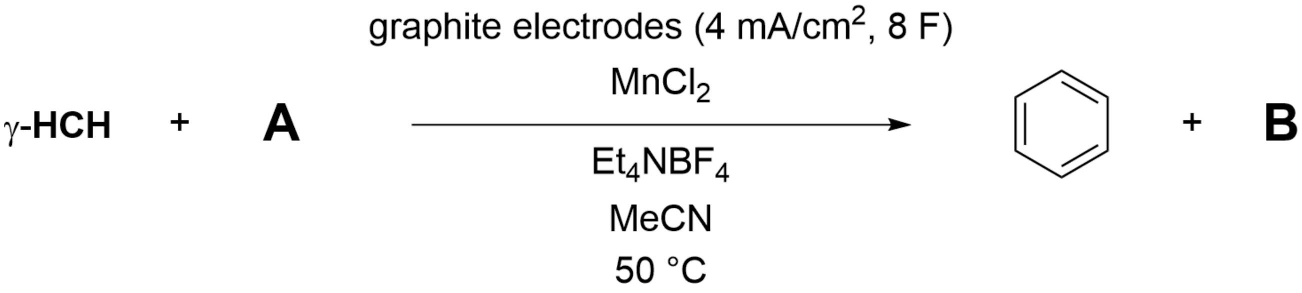
Whilst the γ-isomer of **HCH** was available in >98% purity by this point, this was achieved through purification; the synthesis of **HCH** always gave a complex mixture composed of 65-70% α-**HCH**, 7-10% β-**HCH**, 14-15% γ-**HCH**, 7% δ-**HCH**, 1-2% ε-**HCH**, and 1-2% of the other isomers. Once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



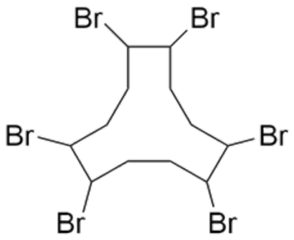
The mass spectrum of compound **B** gave the following ions: m/z 238.125 (100.0%); 239.128 (13.0%); 240.122 (63.9%); 241.125 (8.3%); 242.119 (10.2%); 243.122 (1.3%). Percentages listed show the relative amounts with the most intense peak set at 100%.

(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.

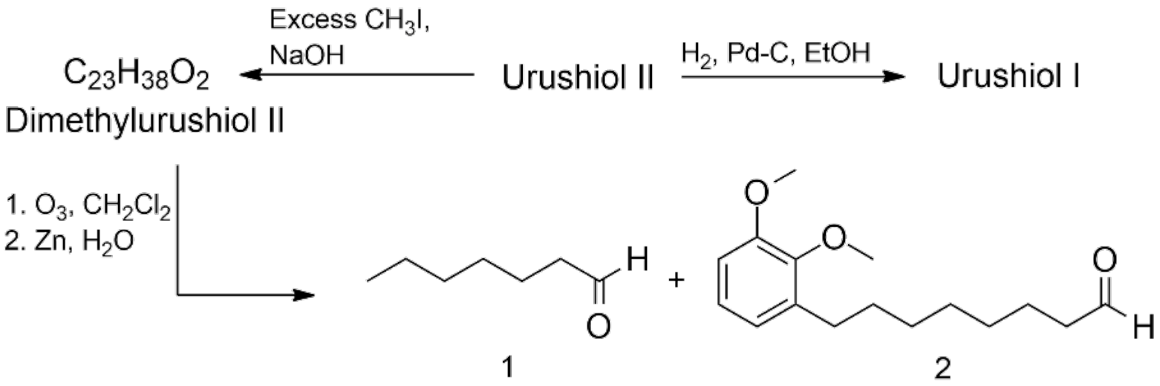
Unlike **HCH**, the **HBCD** commercial product is used as a mixture of isomers. **HBCD** is produced from the bromination of cyclododeca-1,5,9-triene. Four isomers of cyclododeca-1,5,9-triene are possible: (i) all-*cis*; (ii) *cis*,*cis*,*trans*; (iii) *cis*,*trans*,*trans*; and (iv) all-*trans*.

(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?

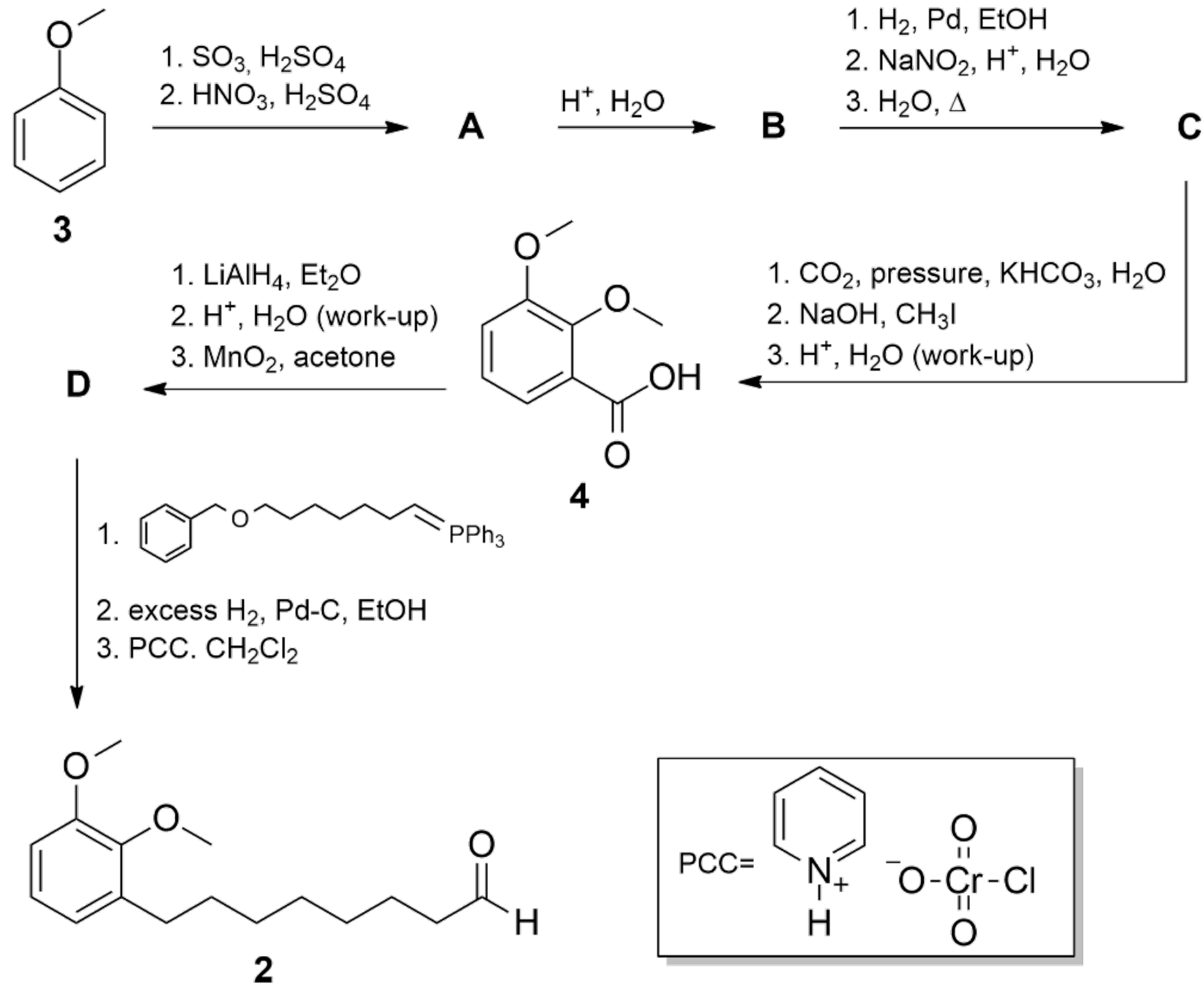
3. Urushiols

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.



(a) **Draw** the structures of **Urushiol I**, **Urushiol II**, and **dimethylurushiol II**.

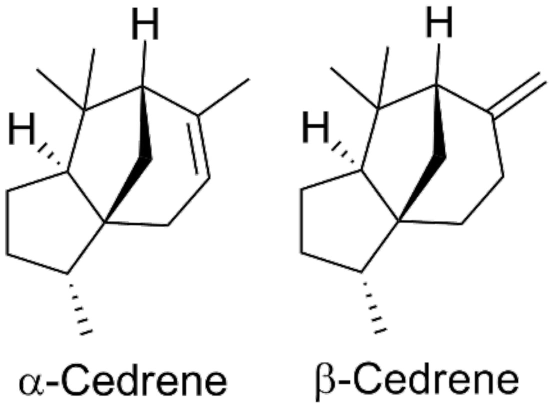
The synthesis of compound **2** is shown below.



(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.

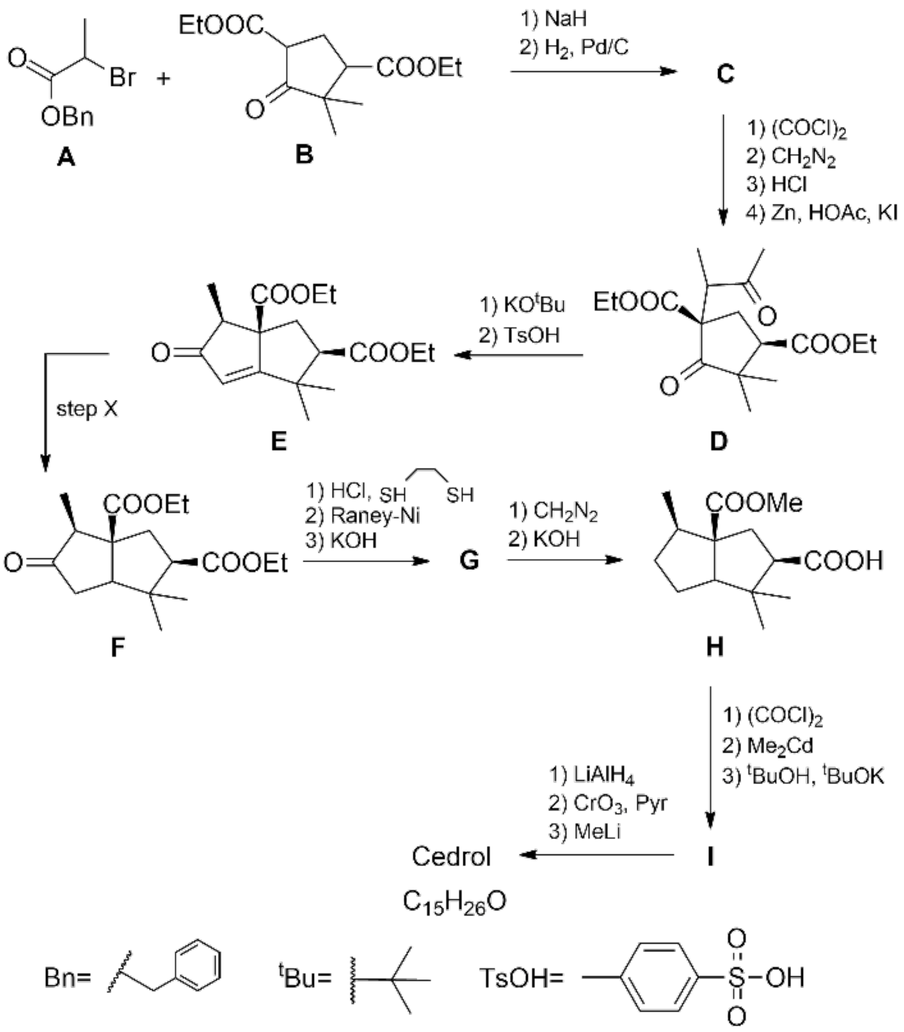


(a) **Circle** the stereocentres in α-cedrene and **assign** them as *R* or *S*.

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

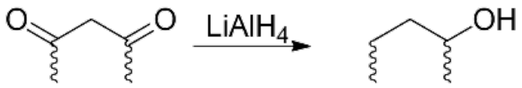
In 1955 Stork *et al.* used an eight step synthesis to make cedrol, a precursor to cedrene. It is possible to convert cedrol to cedrene by adding a sulfate salt. The synthesis of cedrene starts from compounds **A** and **B**.

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



Additional hints:

- Pyr=pyridine;
- $(COCl)_2$ 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.



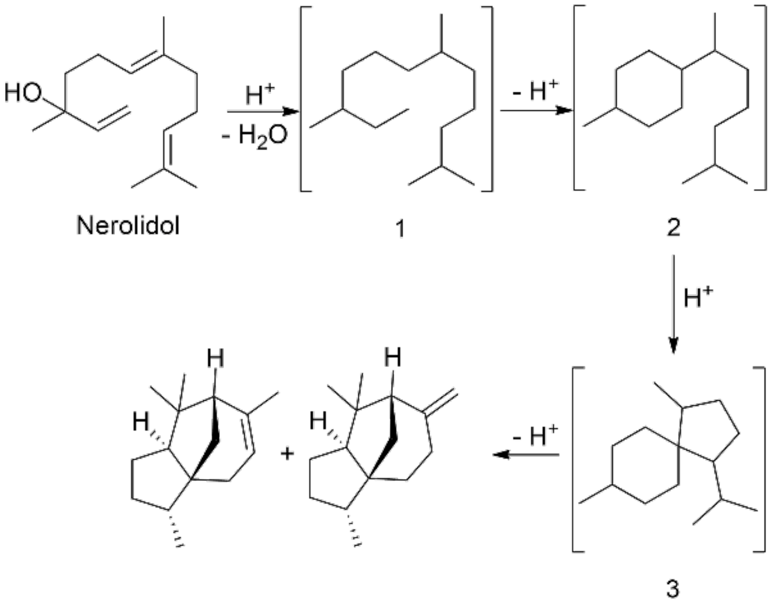
(b) **Draw** the structures of **C**, **G**, **I**, and **cedrol** that are obtained after work-up. You do not need to show stereochemistry.

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

□ Li, NH_3 □ $LiAlH_4$ □ H_2, Pd/C □ HNO_3 □ H_2SO_4

Method 2: Cyclisation of nerolidol

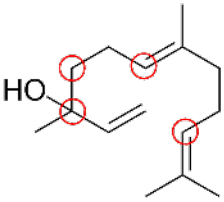
It is also possible to isomerise the structure of nerolidol to both α-, and β-cedrene by adding acid. This will remove the alcohol group and start a cyclisation reaction. The conversion takes place via multiple intermediate structures. Incomplete structures of three of these intermediates are shown.



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.

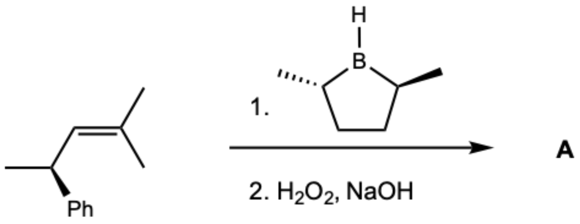


(e) **Circle** the four corresponding carbon atoms in cedrene (α or β) which were circled in nerolidol.

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.

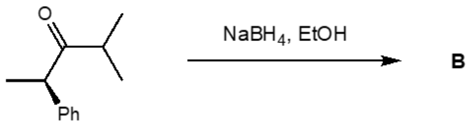
One of the simplest ways to perform a stereoselective reaction is through the use of a chiral reagent.



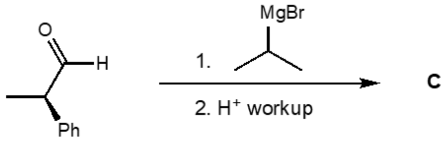
(a) By considering the transition state for the hydroboration reaction across the double bond, **draw** the structure of the major stereoisomer **A**.

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.

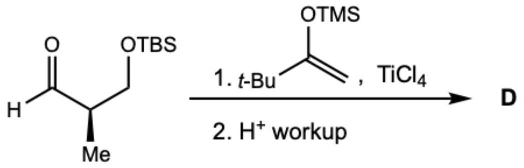
(b) For each reaction, **draw** a Newman projection showing the ideal approach of the nucleophile. Use the labels =O, –H, –Ph, –Me and –*i*Pr. Show the structure of the nucleophile in full.

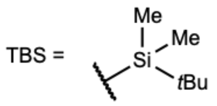
(c) **Draw** the structures of compounds **B** and **C**, indicating the stereochemistry clearly.

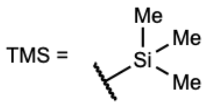
(d) **Which** reaction should you use to synthesise product **A**?

☐ **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:



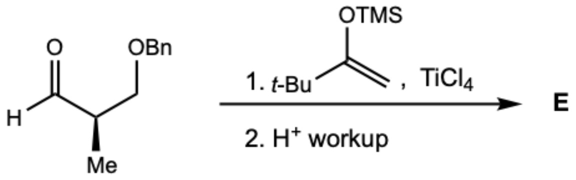


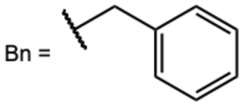


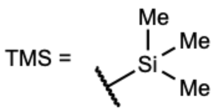
(e) **Draw** a Newman projection showing the ideal approach of the nucleophile. Use the labels =O, –H, –Me, –CH_2OTBS and Nu.

(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.





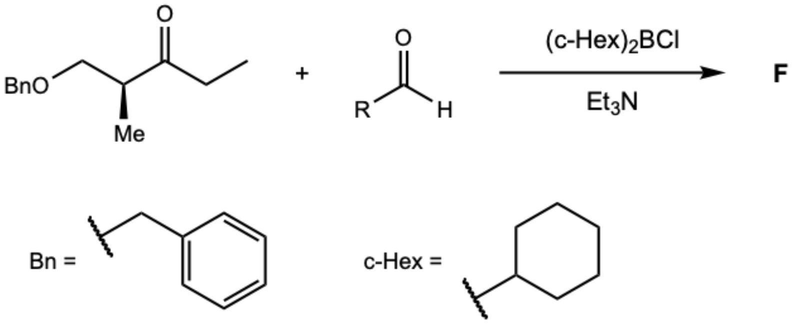


(g) **Draw** a diagram of the transition state in this reaction. *Hint:* It involves the formation of a six-membered ring adopting a half-chair conformation.

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

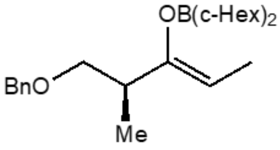
(i) **Why** does the Felkin-Anh model not predict the correct stereoisomer in this example?

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.



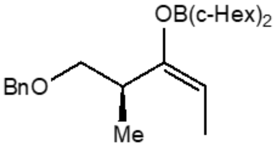
(j) **Determine** the geometry of the boron enolate formed.

a.



(Z) - enolate

b.

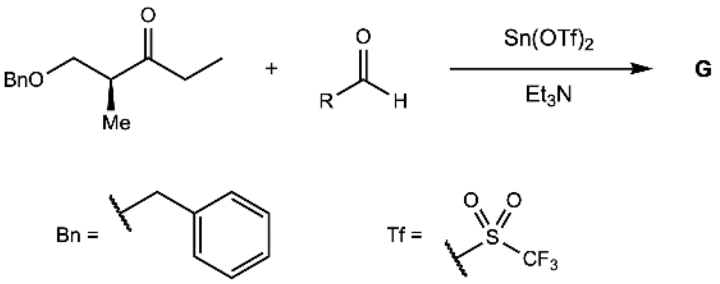


(E) - enolate

(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.

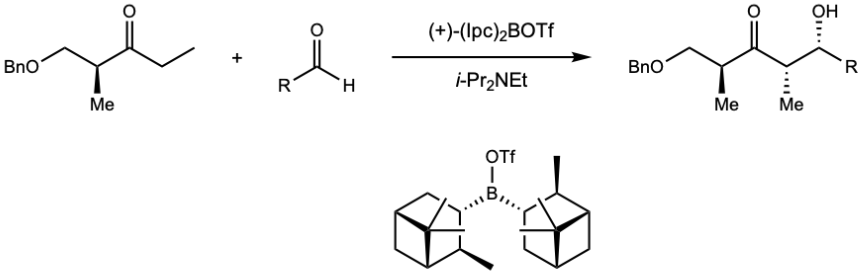
Once again, changing the reaction conditions can lead to the formation of a different stereoisomer.



(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.

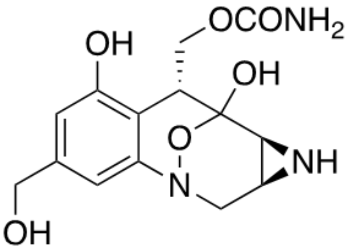
In fact, using a chiral reagent, yet another stereoisomer can be formed selectively.



(+)-(Ipc)$_2$BOTf

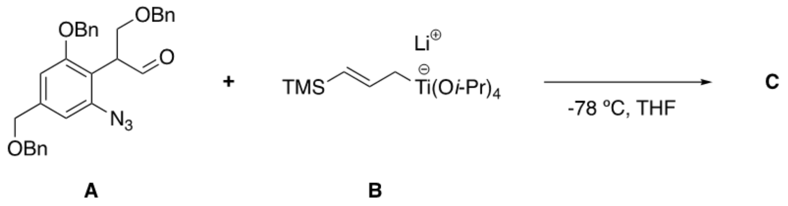
Rationalising the stereoselectivity of this reaction is beyond the syllabus of IChO2025 and left as a challenge to the enthusiastic student!

6. Stereocontrol in the synthesis of FR66979



FR66979

FR66979 was isolated from the bacterium *Streptomyces sandaensis* in 1987. It was first identified as a promising antibiotic, but subsequently found to also possess potent antitumour activity by forming interstrand cross-links in duplex DNA. In this question, we will examine the total synthesis of FR66979 completed in 2002 by Ciufolini and co-workers.



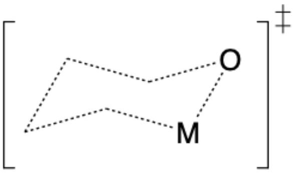
The first step in the synthesis involved the coupling of aldehyde **A** with organometallic species **B** to form **C**.

(a) **Draw** all the possible stereoisomers of **C**.

From what you have learnt in the previous question, not all the possible stereoisomers will be formed in equal amounts. Consider the reaction between (*R*)-**A** and **B**.

(b) **Draw** a Newman projection showing the ideal approach of the nucleophile in this reaction. Use the labels =O, –H, –Ar, –CH_2OBn, and Nu.

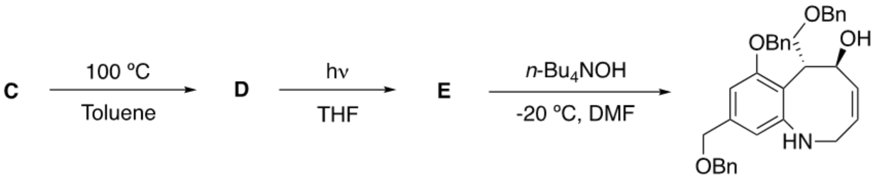
(c) Referencing your answer to part (b), **draw** the arrangement of the reactants as they come together to form the six-membered ring transition state in the reaction to form **C** following the template below. Clearly show the orientation of the stereocentre, using the same labels as in part (b). **Edit** the dotted lines to show the correct bond orders and add substituents as necessary.



(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**.

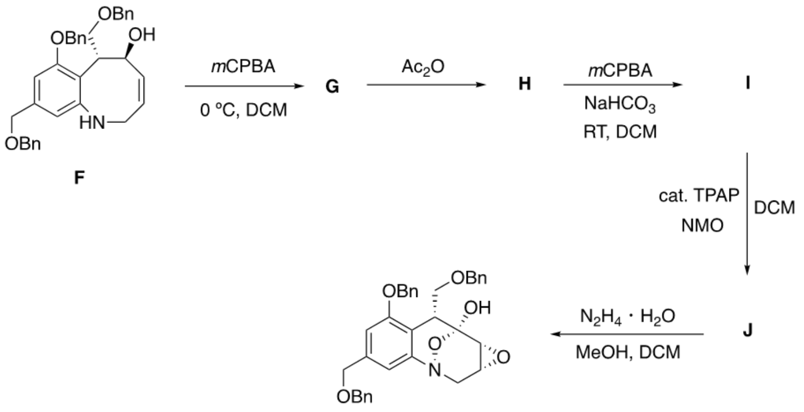
Hint: Nitrogen gas evolved during the photolysis of **D** to form **E**. **D** contained a five-membered ring while **E** contained a three-membered ring.

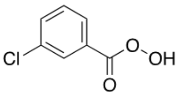


F

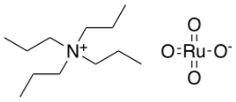
(e) **Draw** the structures of **D** and **E**. You do not need to indicate stereochemistry.

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

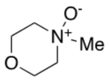




mCPBA



TPAP



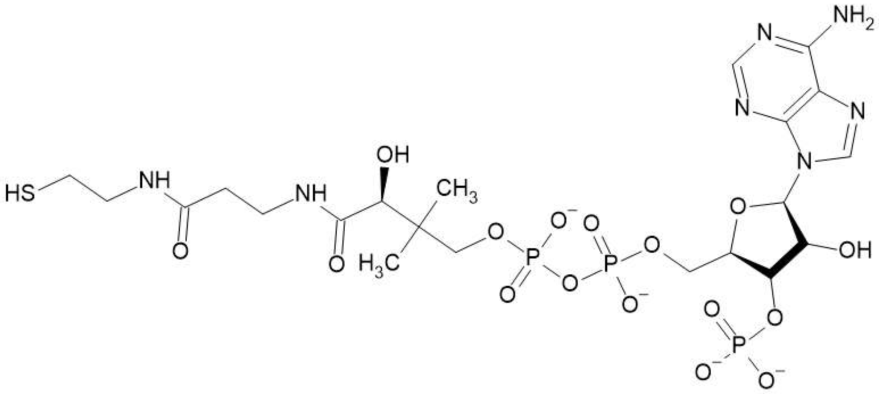
NMO

(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 B_5), and thioethanolamine:



During CoA biosynthesis, vitamin B_5 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 B_5 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**.

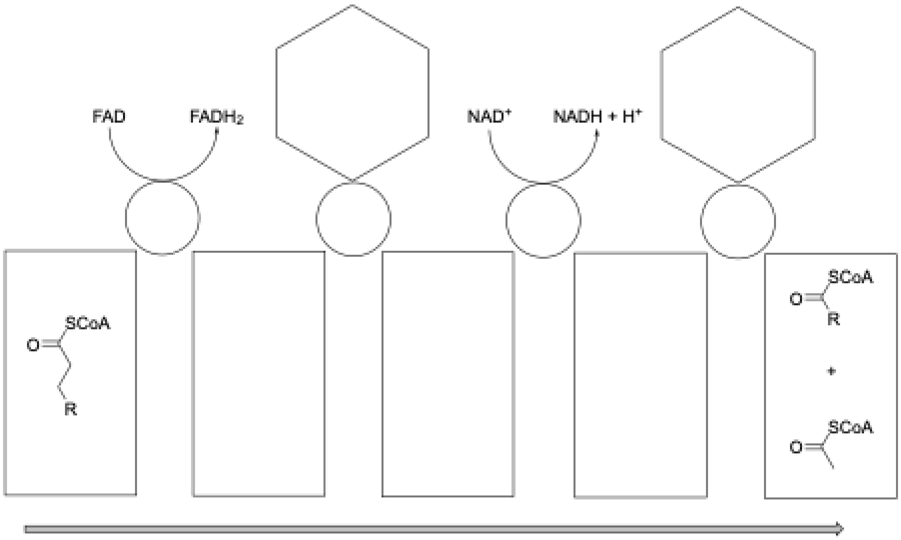
(b) **Draw** the structures of **X2-X4** and pantoate.

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-ketothioester
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)NH_2 –NH_2 NH-C$(NH_2)_2^+$ –SH -S-CH_3

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 E_1-E_4 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.

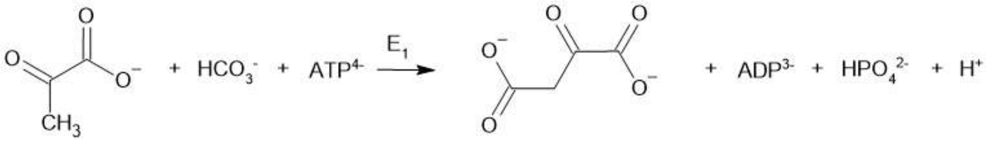
iv) Lyases – Non-hydrolytic addition or removal of groups from substrates, with C-C, C-N, C-O, or C-S bonds cleavage in the latter case.

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.

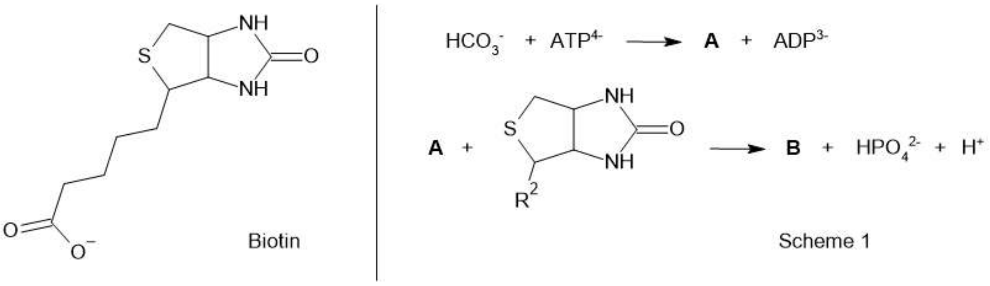
Hint: enzymes catalyse both forward and reverse reactions.

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



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

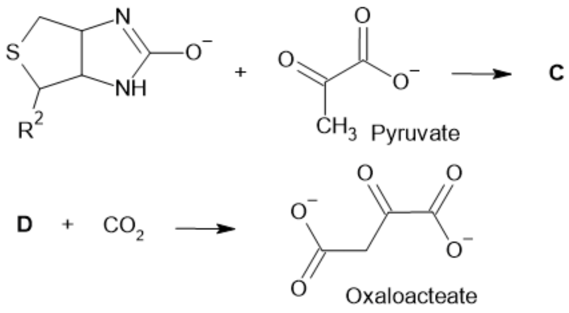
Biotin (see below) covalently bound to a lysine (Lys) residue is the co-factor found in the active site of E_1. The reaction develops in two subsites, one being responsible for the biotin carboxylation (**Scheme 1**) and the other for CO_2 attachment to pyruvate.



(h) **Write** the reaction between biotin and the Lys residue (show the latter as R^1-$(CH_2)_4$-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 CO_2 (**Scheme 2**):



Scheme 2

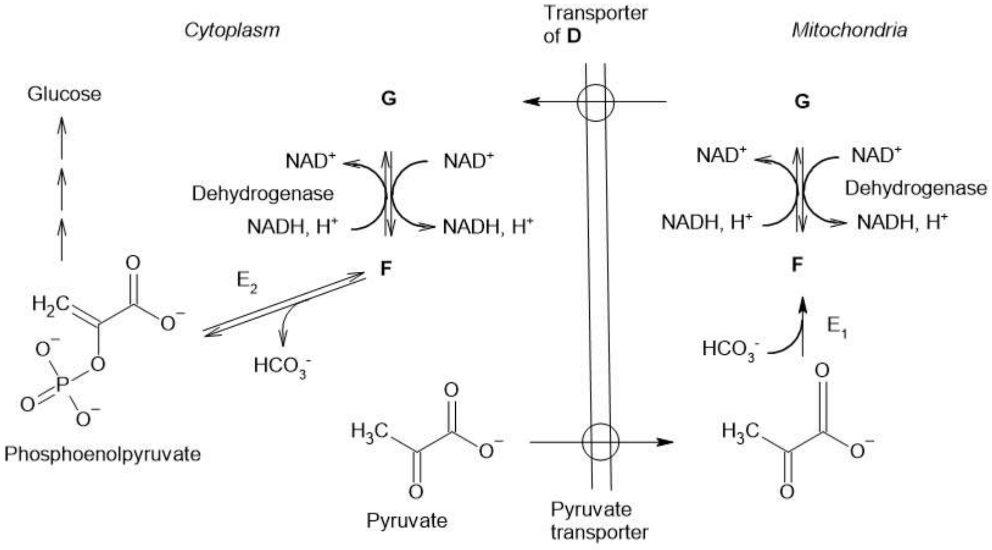
(j) **Draw** the structures of **C** and **D.**

E_2 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 E_2 catalysed reaction.

(l) **What class** does E_2 belong to?

E_2 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).



Scheme 3

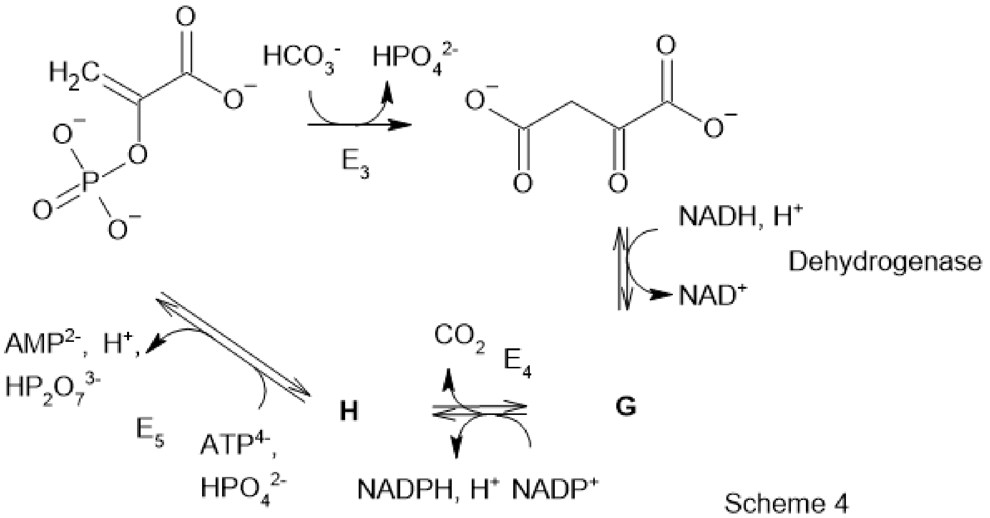
(m) **Draw** the structures of **F** and **G**.

CO_2 (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 $^{14}CO_2$ enters the carboxylation reaction instead of $^{12}CO_2$. However, some trace amount of labelled glucose is detected in actual experiments with $^{14}CO_2$.

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

Hint. Some substances are intermediates of several metabolic pathways.

E_3 and E_4 are involved in the metabolic cycle found in some plants (**Scheme 4**).



Scheme 4

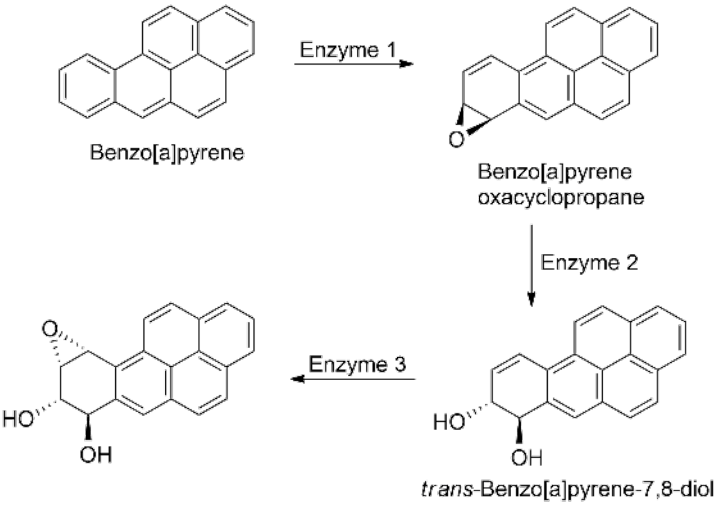
(o) **Draw** the structure of **H**.

(p) **What class(es)** do E_3 and E_4 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.

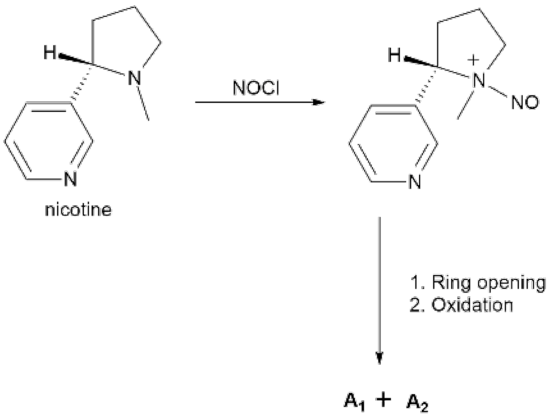
(c) **Determine** the absolute stereochemistry of all of the stereocentres in the product of the conversion above and assign them as *R* or *S*.

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.

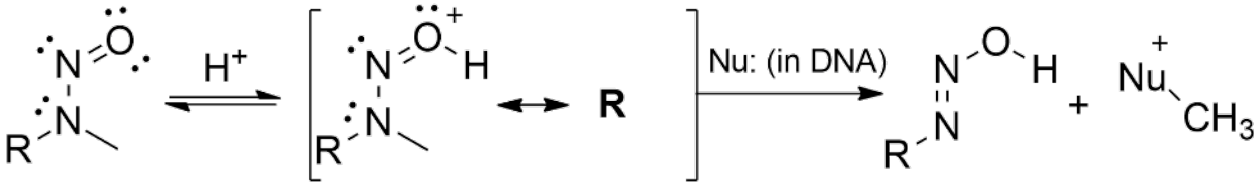
Nicotine is not only a compound that causes the above to happen. It is a known 'tumour enhancing' compound. Nicotine can also react to form two compounds that are both carcinogenic. This happens in the following way:



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

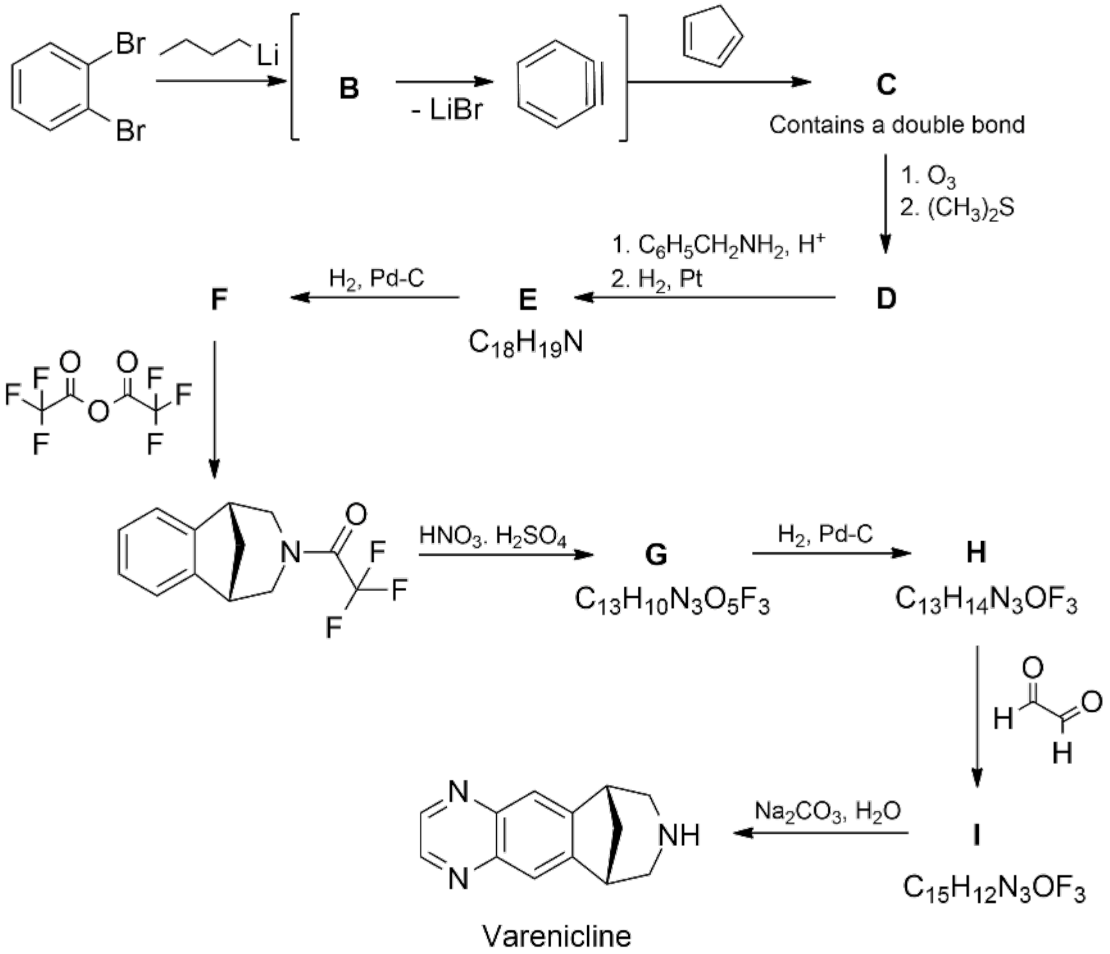
(e) **Draw** the structural formulae of **A1** and **A2**.

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.

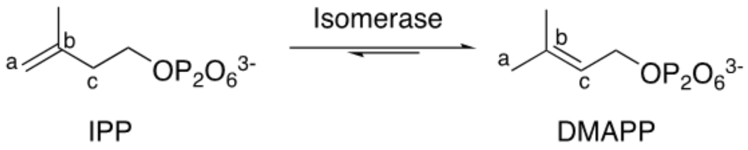


(g) **Draw** the structures of compounds **B-I**.

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.

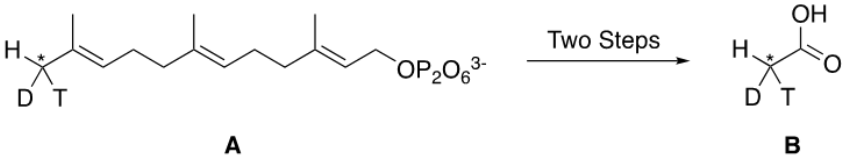
In this question, we will focus on one particular enzymatic transformation: the isomerisation of isopentenyl pyrophosphate (IPP) to dimethylallylpyrophosphate (DMAPP), by the enzyme isopentenyl pyrophosphate isomerase.



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 (^{3}H, T). The isomerase reaction was carried out in D_2O, such that a deuterium (^{2}H, 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.

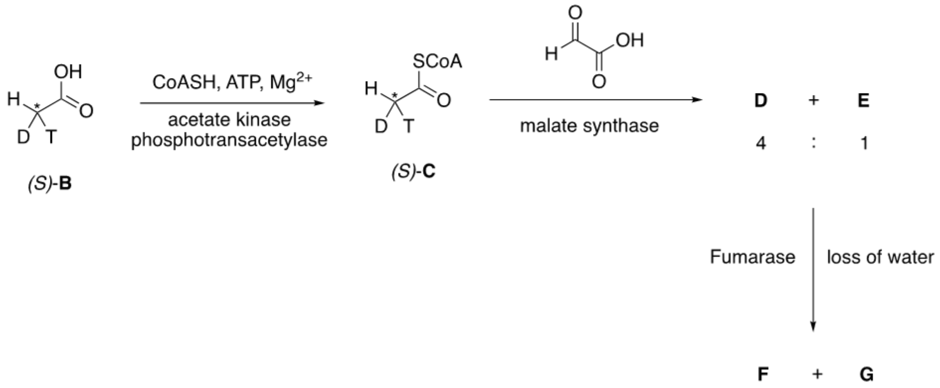


(a) **Suggest** a suitable two-step sequence of reactions that can convert chiral product **A** to chiral acetic acid **B**.

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.

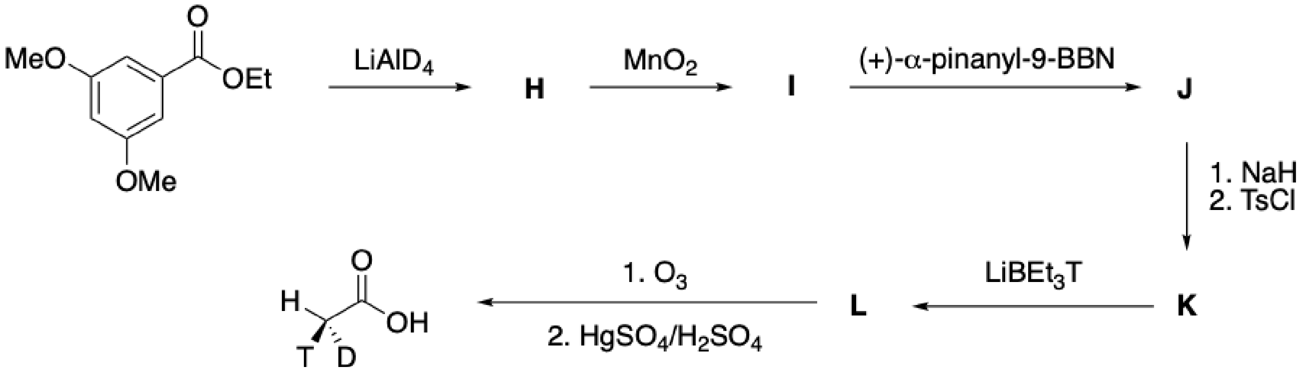
The amount of tritium can be determined by measuring the radioactive activity. A ratio *Z* is defined as:

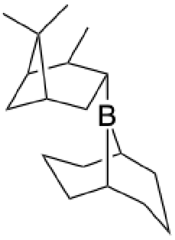
$$\boldsymbol{Z} = \frac{\text{T activity after fumarase}}{\text{T activity before fumarase}}$$

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

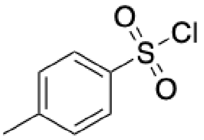
(g) Similarly, **determine** the value of ***Z*** for (*R*)-**B**.

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.





(+)-α-pinanyl-9-BBN



TsCl

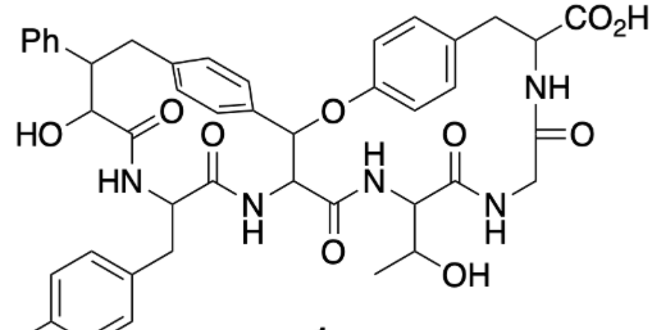
(h) **Draw** the structures of **H**, **I**, **J**, **K**, and **L**, clearly showing the stereochemistry.

(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

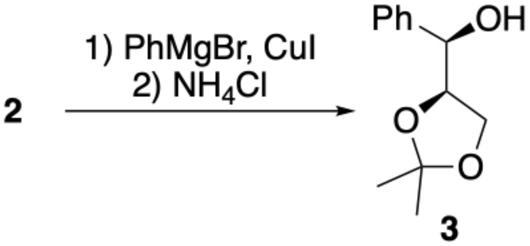
Total syntheses of natural products are rarely performed to acquire a commercial route to a physiologically active compound of value. Rather, total syntheses are often carried out to show that they can be done or they are carried out to prove the structure of the natural product, especially its stereochemistry, 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.



1

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

The total synthesis starts with the reaction presented below.



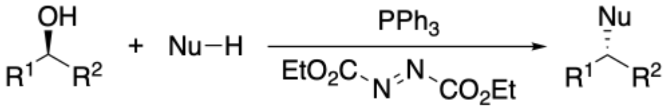
3

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

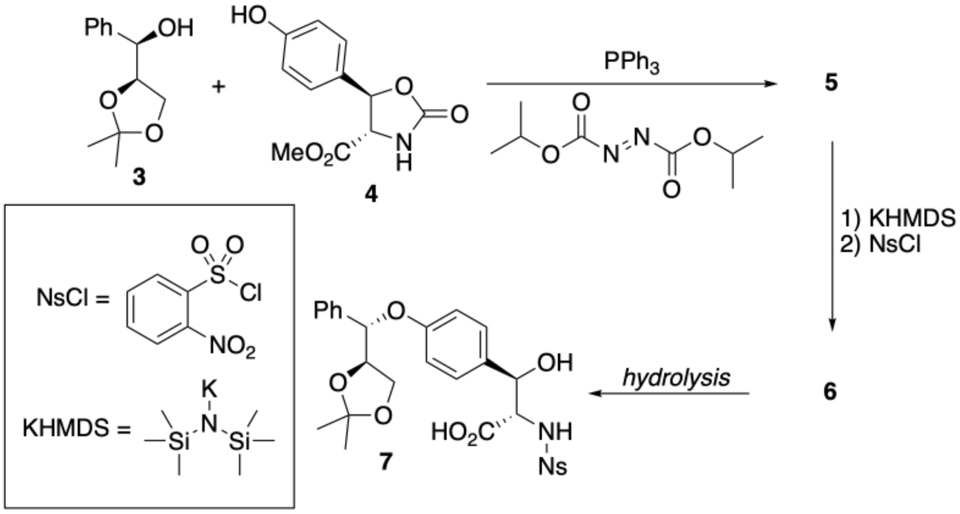
(c) **Choose** the model that can be used to predict the stereochemistry of product **3** starting from compound **2**:

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.

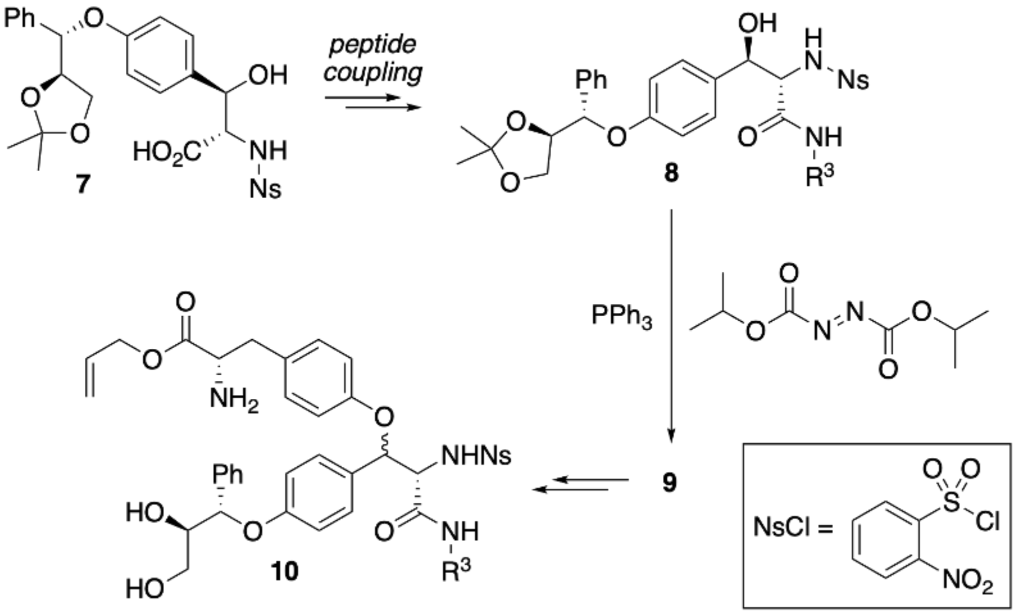


This reaction was used in the aforementioned total synthesis as demonstrated in the scheme below.



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

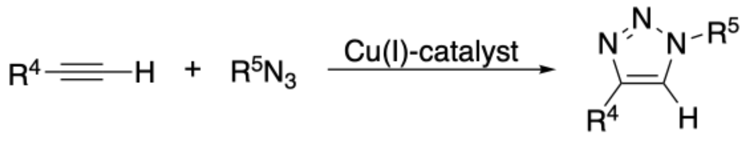
Further steps of the synthetic pathway included compounds **8**-**10**.



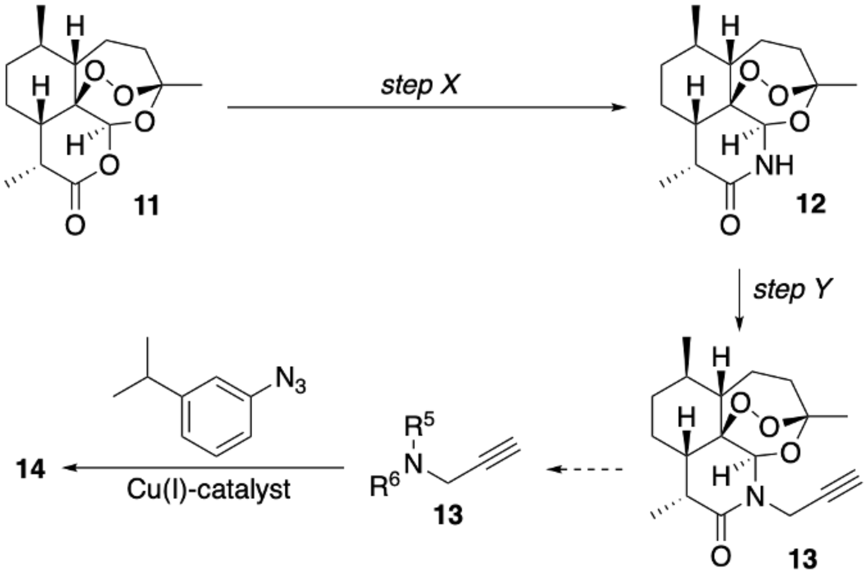
(e) **Draw** the structure of **9** including its absolute stereochemistry. *Hint:* **9** is a stable compound without any charge separation.

Derivatisation of a natural product

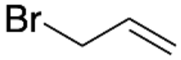
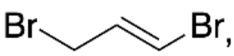
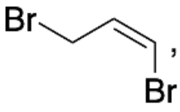
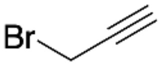
R. Huisgen (1920-2020) established the field of 1,3-dipolar cycloaddition (Huisgen cycloaddition). The azide-alkyne cycloaddition (AAC) is a reaction that gives easy access to triazoles. It is used to do various diversifications of compounds containing an alkyne fragment. K. B. Sharpless and M. Meldal 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 Leuwen, 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.



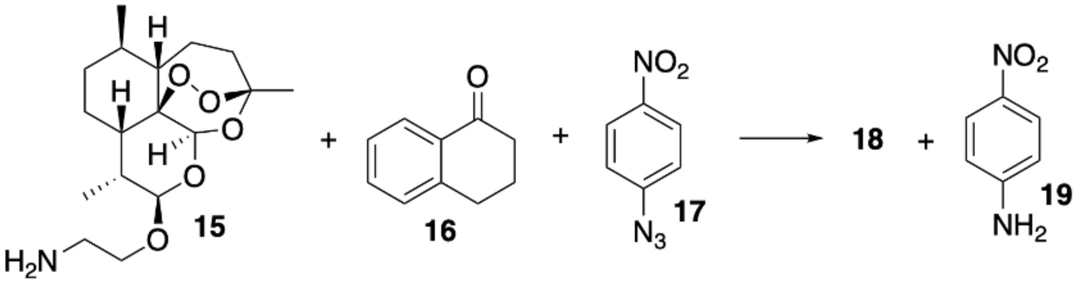
(f) **Choose** the appropriate reagent(s) for steps X and Y from the table below.

Reagent	Step	Reagent	Step
NMe_4Cl, H_2O		 , NaOH	
NH_2OH		 , NaOH	
NH_3 (liquid)		 , NaOH	
NH_2NH_2		 , 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.

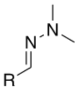


(h) **Draw** the structures of **18**, **20**, and **21**. You may use an abbriviation for **15** such as RNH_2.

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?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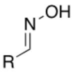
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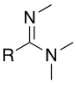
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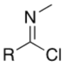
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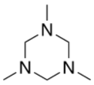
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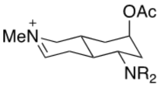
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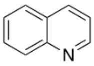
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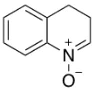
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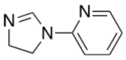
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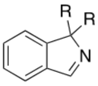
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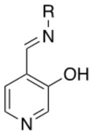
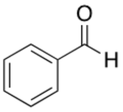
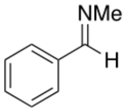
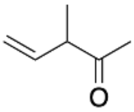
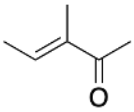
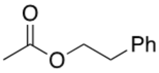
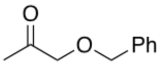
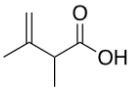
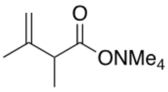

12

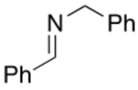
(a) From the structures above, **choose** those that have an imine functional group (assume that R is an alkyl group).

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

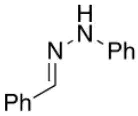
 **13**	 **14**	 **15**	 **16**
 **19**	 **20**	 **21**	 **22**

(b) From the pairs of compounds above, **choose** the compound that shows the highest wavenumber (cm^{-1}) for the C=X group (X = 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.



23

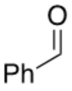


24

(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.



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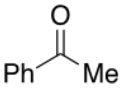


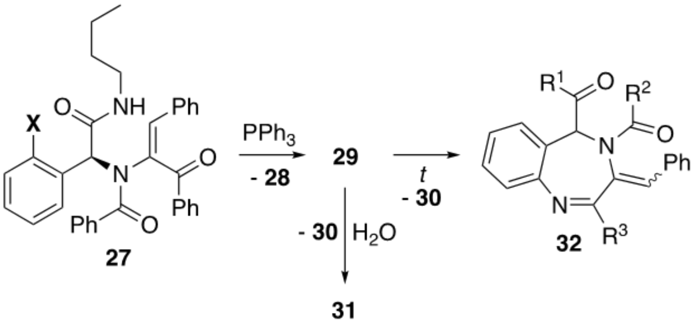
26

(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.

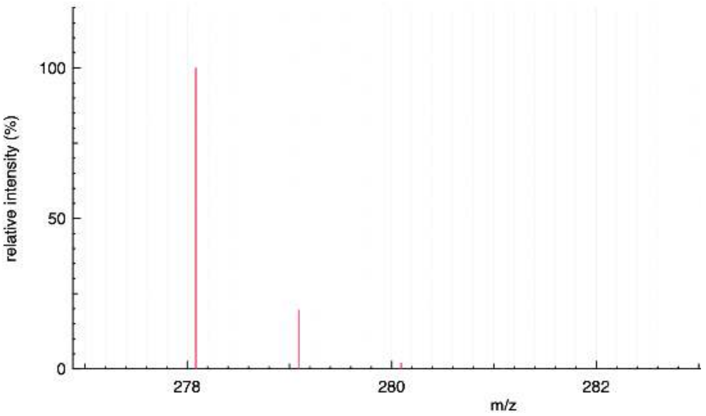
Condition(s) for **25**:	Condition(s) for **26**:

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**.

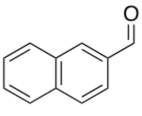


(f) **Draw** structures **27-32** including absolute stereochemistry. *Hints:* **X** is a functional group. Compound **27** can react with phenylacetylene (this reaction is catalysed by copper(I) iodide), and the reaction generates a five-membered ring that contains three nitrogen atoms. The mass spectrum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

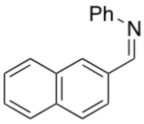
MS of **30**



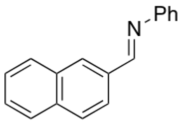
Imines and similar compounds sometimes have peculiar stereochemical properties.



33



34



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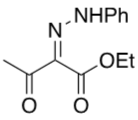
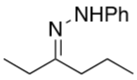
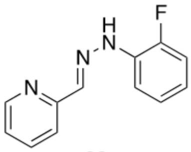


36



37



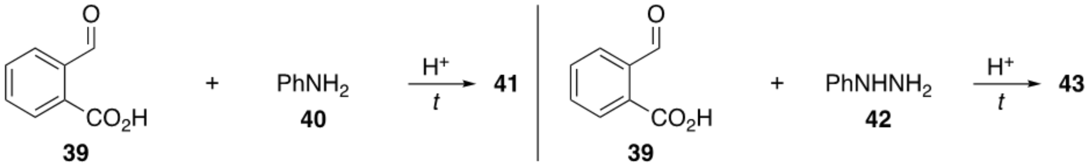
38

(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.

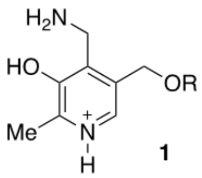


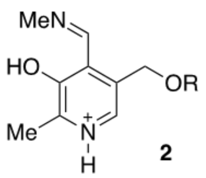
t = heating

(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**.


1

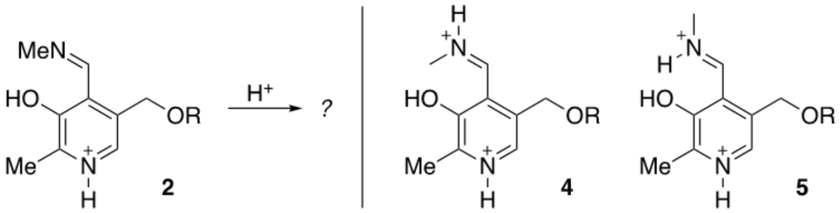

2

(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.

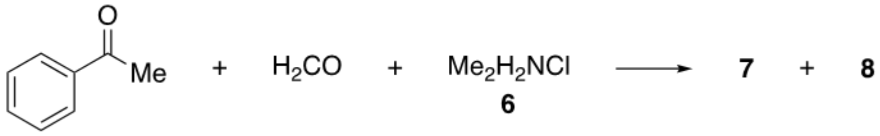
(j) **Draw** a second tautomeric form of **2**. **Draw** a resonance structure of this tautomeric form (the resonance structure should not have charge separation).

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.

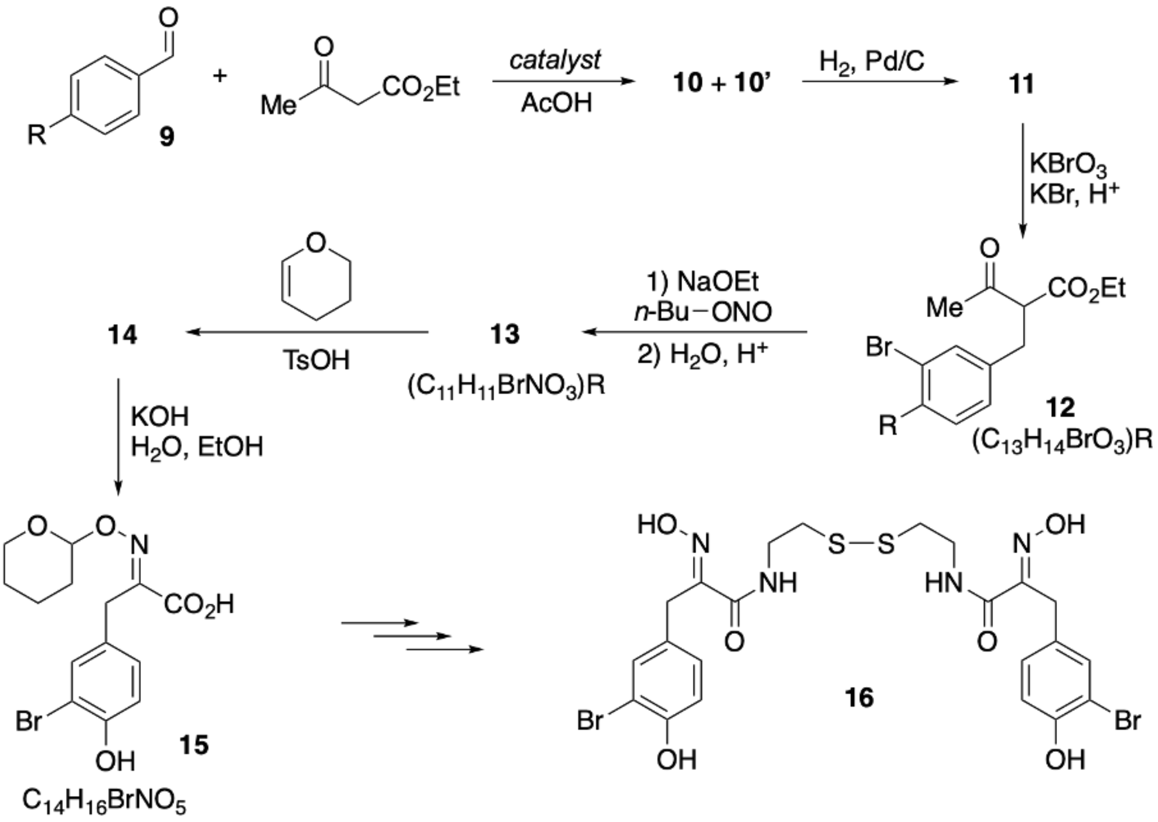
Another way to make an iminium salt is reaction of a carbonyl compound with a secondary amine. In the example below, compound **6** is premixed with a more electrophilic carbonyl compound, and then a second compound with a carbonyl group is added after iminium formation. As a result, products **7** and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

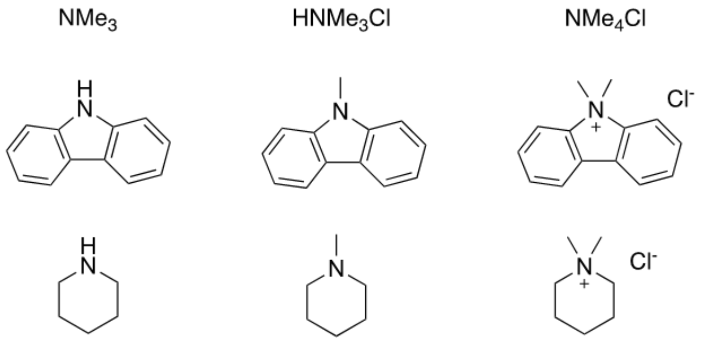


(n) **Write** the unknown substituent R in compound **9**.

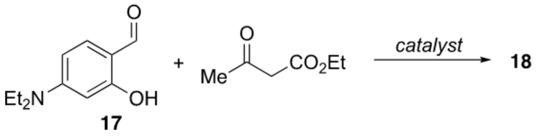
(o) **Draw** the structures of compounds **10**, **10′**, **11**, and **14**. You may use the abbreviation R as shown in the scheme.

(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** <u>cannot</u> 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.



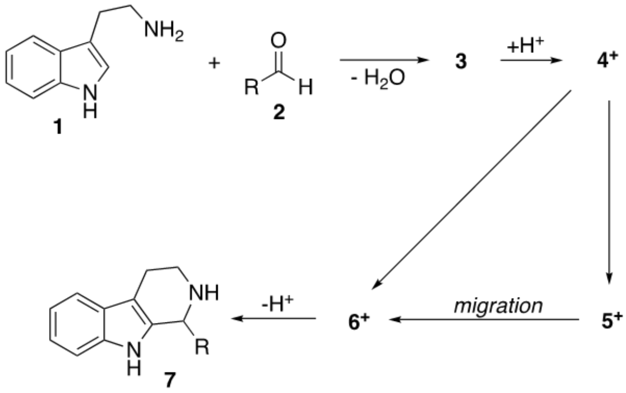
Unlike compound **9**, compound **17** gives only product **18** when it reacts with ethyl acetoacetate under the same catalytic conditions.



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

12. Imine`s guide to the biochemical galaxy

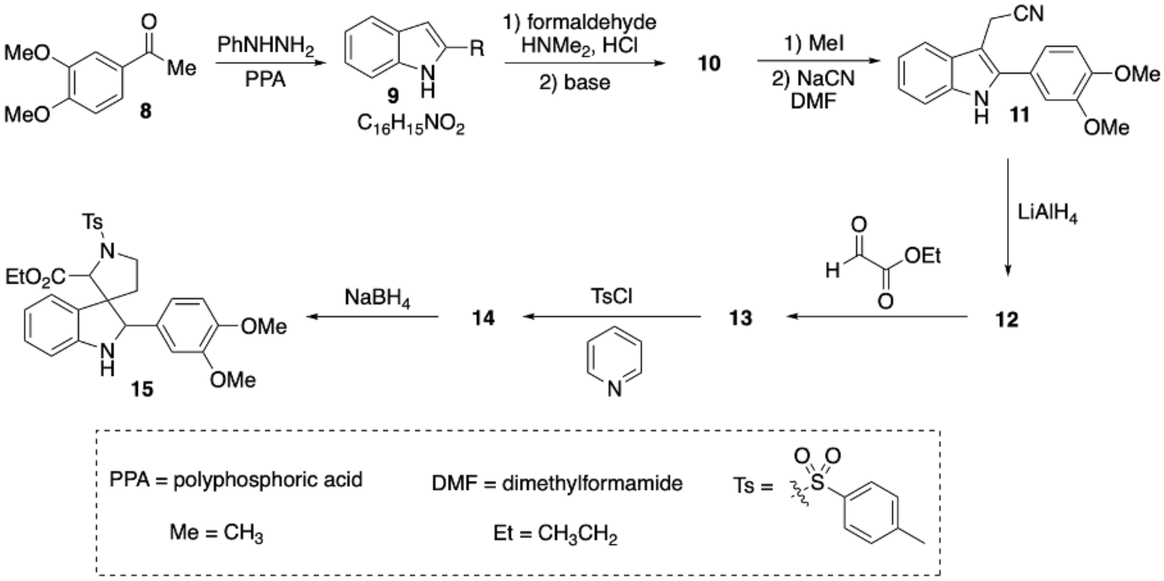
Imines are abundant chemicals both in the laboratory and in nature. Numerous organic reactions have been developed that utilise imines. One example is reaction X, for which the simplified mechanism is shown below (reaction X is the same reaction throughout this task). It is initiated by formation of **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.



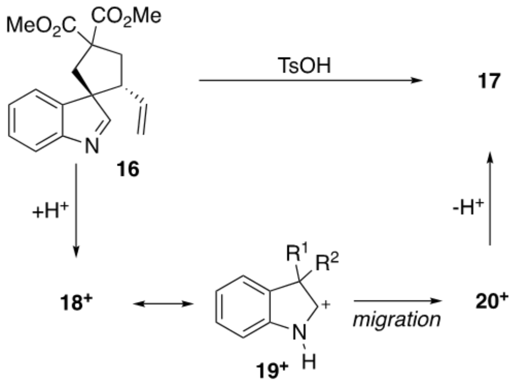
(c) **Draw** the structures of **9**, **10**, and **12**-**14**. Stereochemistry is not important in this part of the task. *Hint:* substituent R is a disubstituted aromatic ring.

(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.

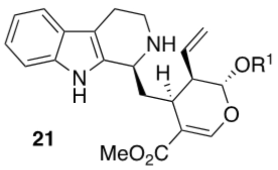
(e) How many stereoisomers does compound **15** have?

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.

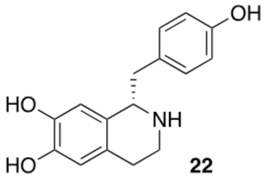


(f) **Draw** the structures of **17**, **18$^+$**-**20$^+$**. **18$^+$** and **19$^+$** are resonance structures. **Specify** the absolute stereochemistry where necessary.

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.



21



22

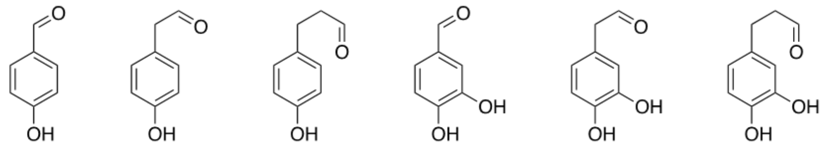
(g) **Suggest** a biochemical pathway for the syntheses of both **21** and **22** using a pair of starting materials from those listed below: **choose** one amino acid and one aldehyde. The pathway should not exceed four steps; consider imine formation and reaction X as two separate steps.

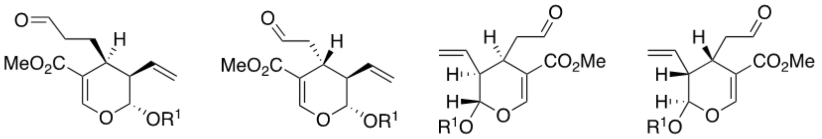
Specify the enzyme for each step using the following abbreviations:

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

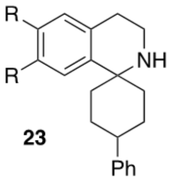
Amino acids:

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

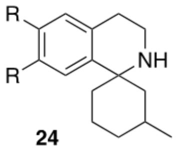




Compounds **23** and **24** can be synthesised by reaction X which is enzymatically catalysed. In this case, only one isomer is obtained out of many stereoisomers.



23

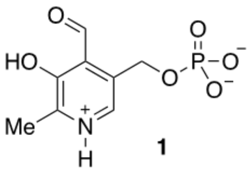


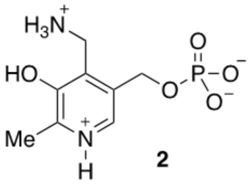
24

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

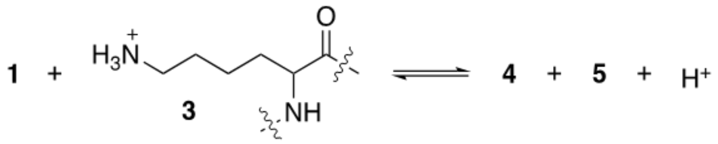
13. Schiff bases, the Universe, and biochemistry

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 B_6, 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**).



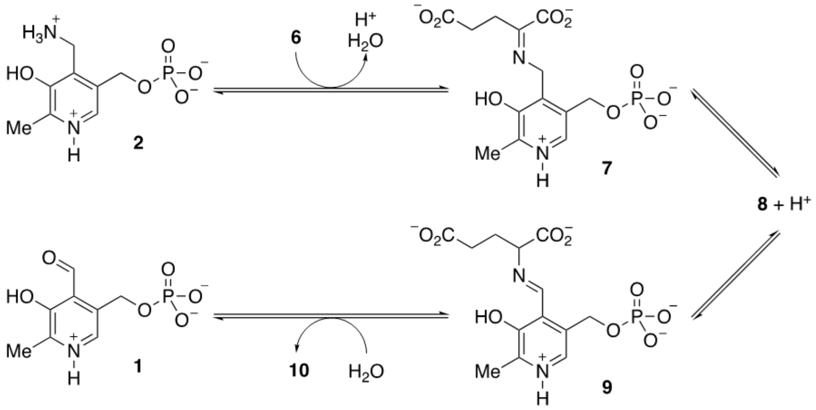


In many enzymes, the reactive aldehyde group of PLP does not exist in the free form. Instead, it forms a Schiff base product (**4**) with a specific lysine residue of an enzyme.



(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 E_1, 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 E_1 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).

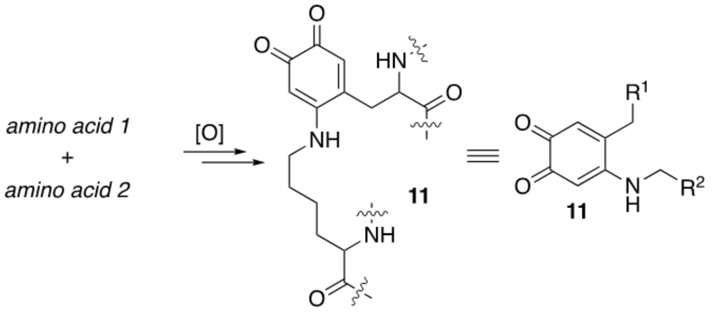
a. Steric hindrance due to the tetrahedral environment of the α-carbon atom.
b. Steric hindrance due to the planar geometry of the quinoid intermediate.
c. Being electron deficient, the pyridinium ring withdraws electron density from the α-carbon atom.
d. Being a strong nucleophile, the pyridinium ring attacks the carbonyl atom of the amino acid.
e. Being a strong electrophile, the pyridine nitrogen atom attacks the carbonyl carbon of PLP.
f. 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 E_2. Its cofactor (quinone **11**) is formed inside the active site of the enzyme from residues of two amino acids as shown below.

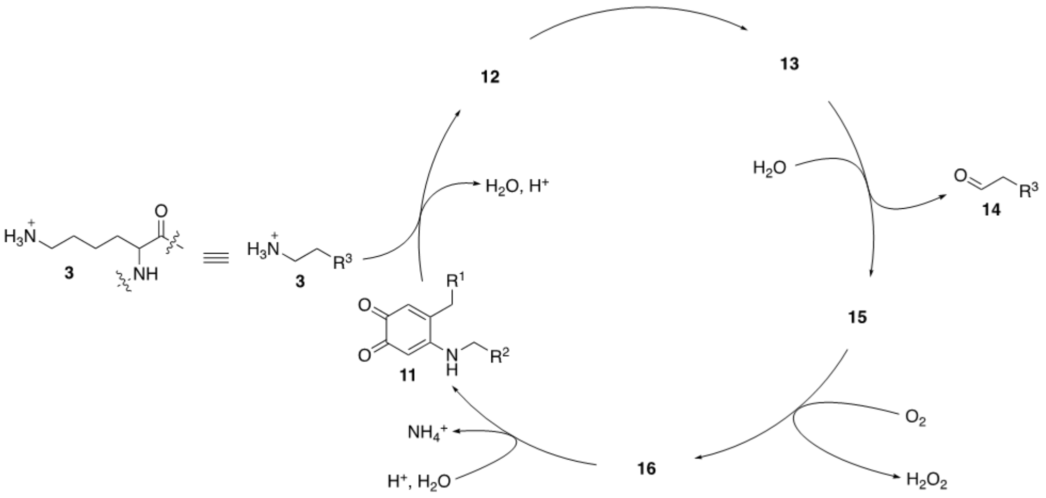


(f) **Select** which amino acid residues were used in the biosynthesis of **11**.

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.



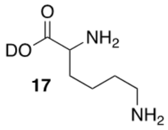
(h) **Draw** the structures of **12**, **13**, **14**, and **16**. Use the simplified formulae of **3** and **11** given above.

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.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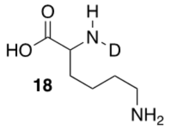
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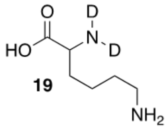
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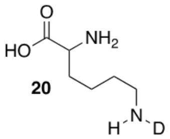
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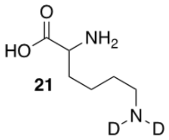
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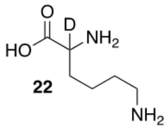
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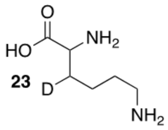
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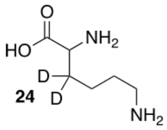
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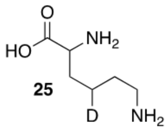
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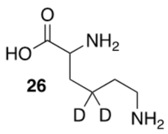
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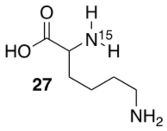
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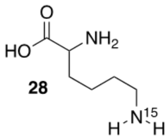
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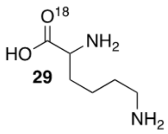
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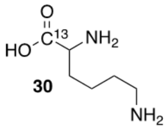
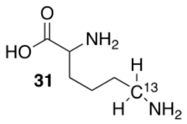

30

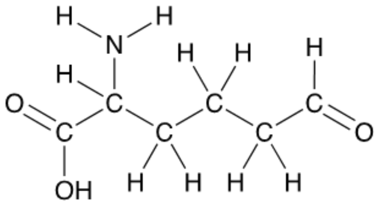

31

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**.

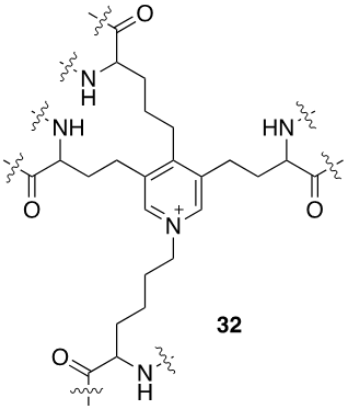
(j) **Draw** the structures of intermediates **34** and **35**.

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

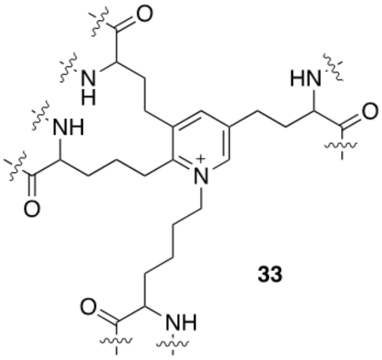
(k) **Circle** the labelled carbon atom in allysine which originated from e-labelled lysine.



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



32



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.

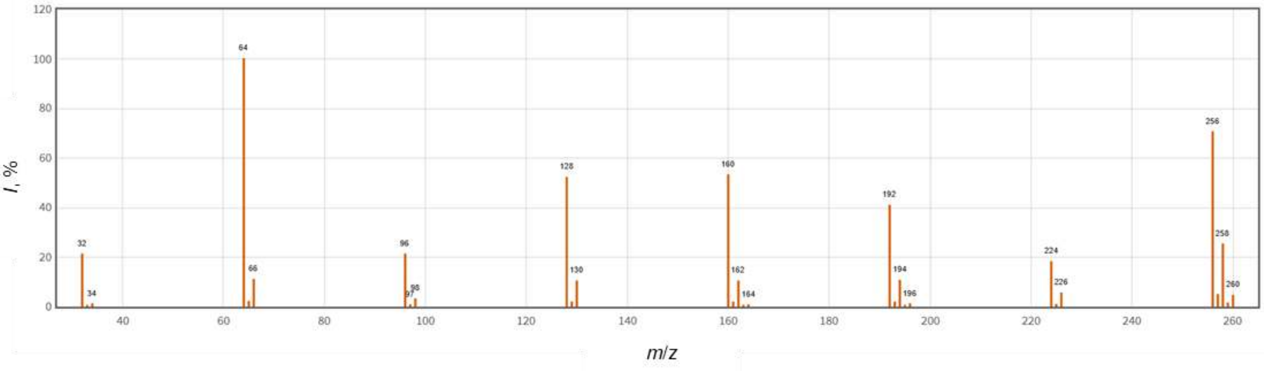
The refining process essentially starts with *atmospheric fractional distillation*, where crude oil is separated into fractions according to their boiling points. After this step, the residual oil is further separated using *vacuum fractional distillation* into heavier fractions with higher boiling points.

(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**. $^{1}/_{3}$ of **A** obtained is then oxidised with air, producing gas **B**, which further reacts with the remaining $^{2}/_{3}$ 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 “isomerate” 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, isomerate, reformate, 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.

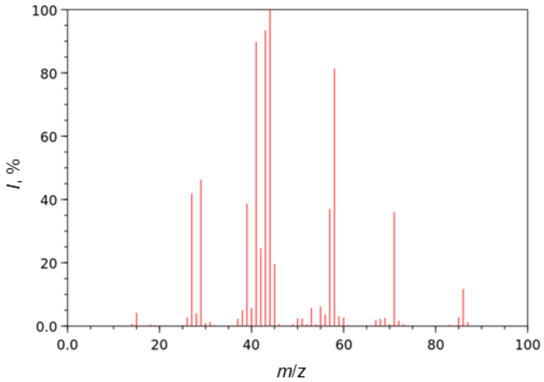
(h) **Determine** the element **Y**, substances **F** and **G**, and **write down** the reaction between Na**Y** and **G**.

15. In search of an oasis in the desert

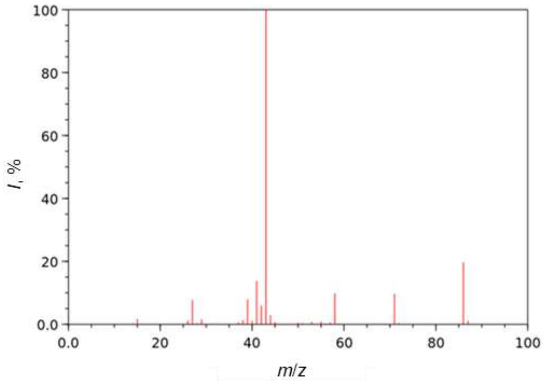
The United Arab Emirates University is located in the city of Al Ain, which is known for its rich history and lush greenery thanks to the largest oasis in the country. Just like searching for an oasis in a desert, in this problem, you will be challenged to find the structures of eight isomers from the 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, % – relative intensity) of these compounds and the wavenumber of the strongest band in their IR spectra are given:

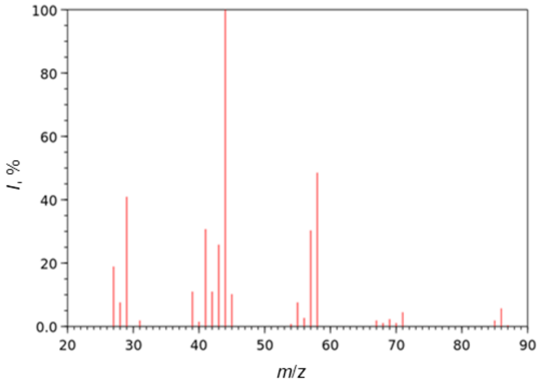
A (1728 cm^{-1})



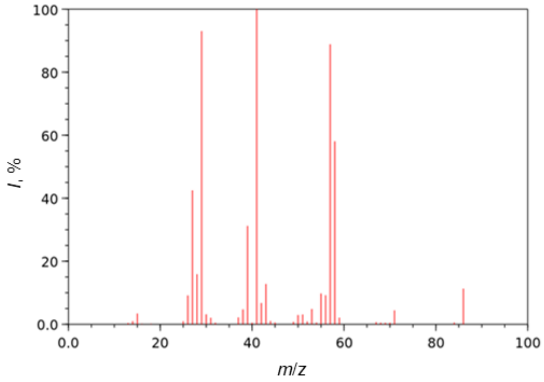
B (1717 cm^{-1})



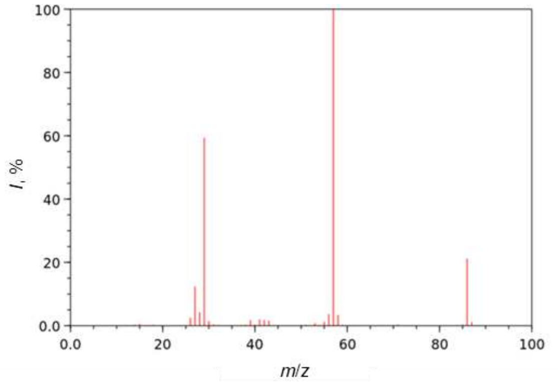
C (1727 cm^{-1})



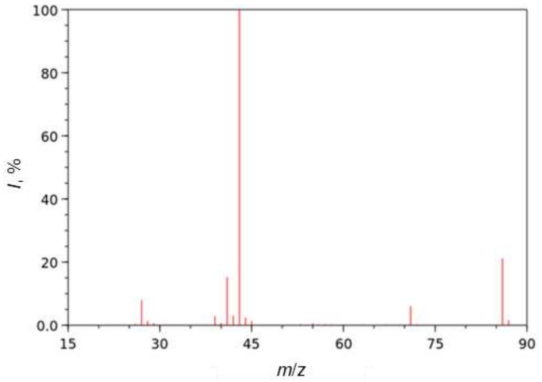
D (1728 cm^{-1})



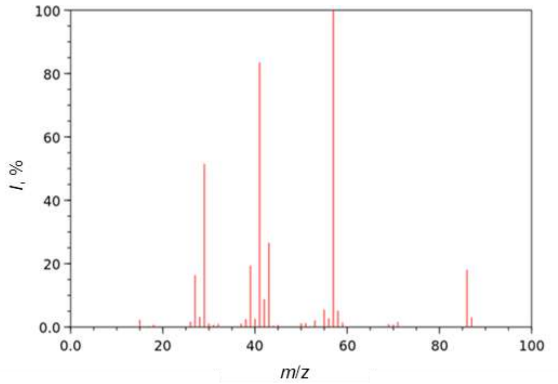
E (1720 cm^{-1})



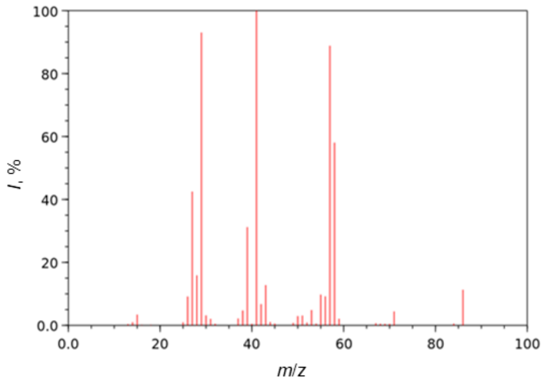
F (1718 cm^{-1})



G (1728 cm^{-1})

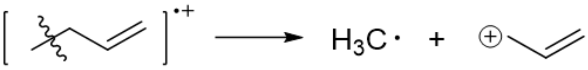


H (1728 cm^{-1})

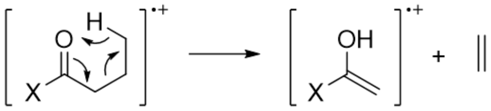


(a) **State** all the possible functional groups (or combinations of functional groups) that molecules with the molecular formula $C_5H_{10}O$ can have.

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:



$X = H, R, OH, OR, NR_2$

(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:

$$v + f = \mathrm{e} + 2$$

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*).

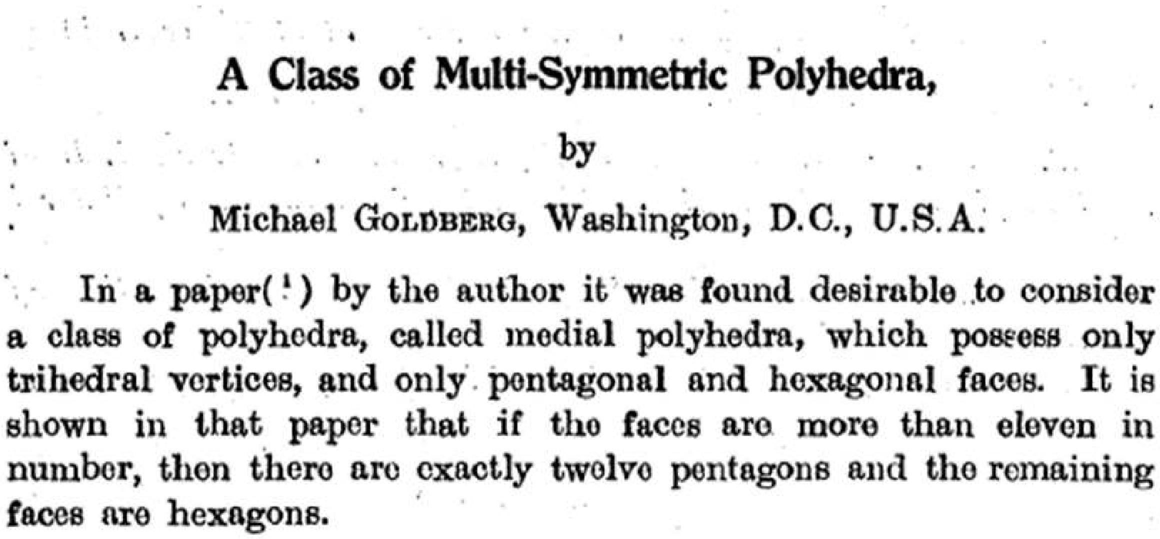
(a) In terms of *n*, **derive** an expression for the number of edges in a fullerene.

(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,

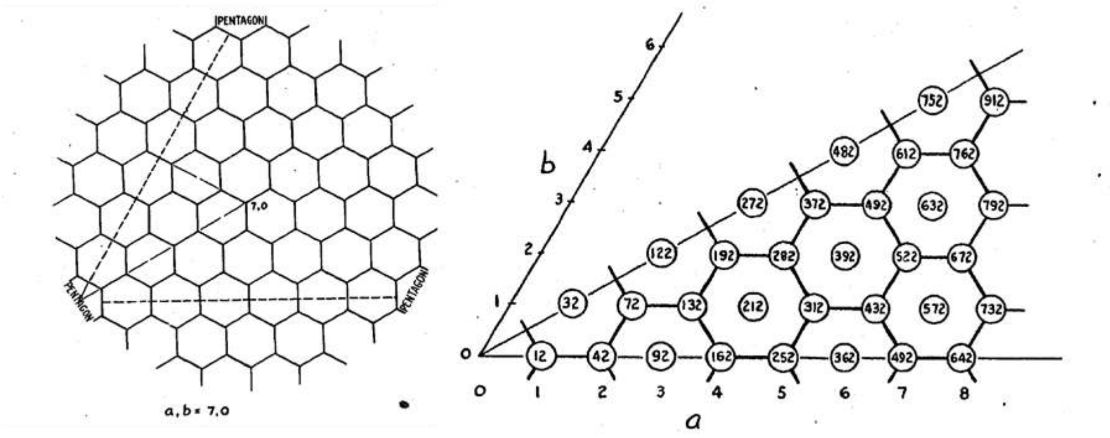
by

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.

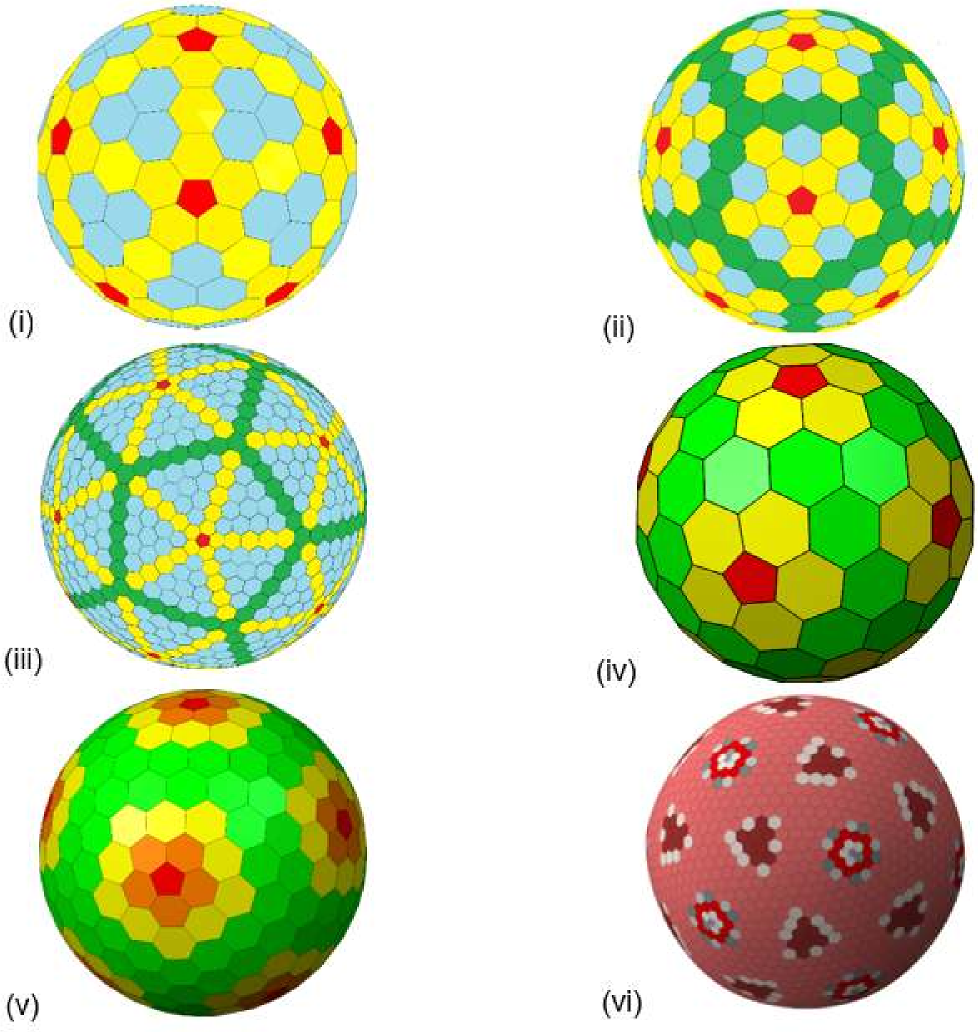
(a,b)	$v = n$	e	f	h
(1,1)				

(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)

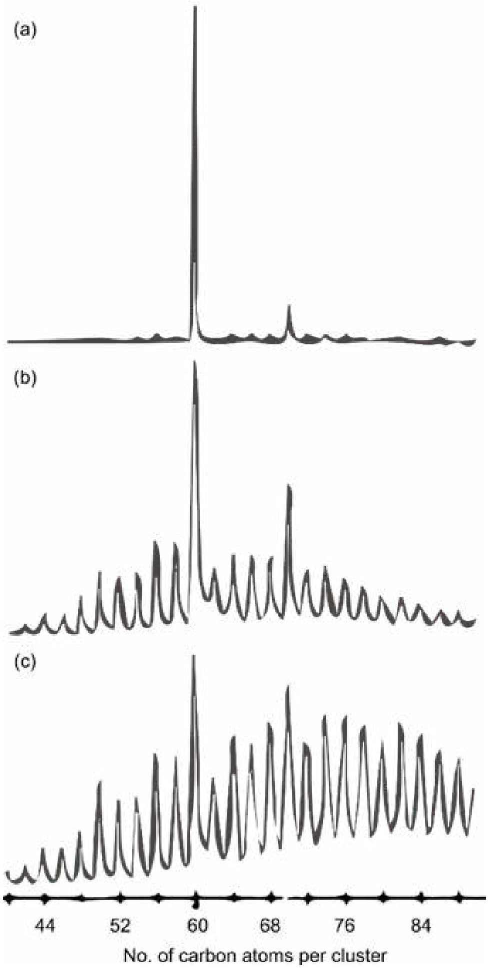
(ii) (7,0) and (5,3)

(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 $^{12}C_{60}$:$^{12}C_{59}{}^{13}C$ peaks.

(j) In the mass spec of C_{70}, **determine** the ratio of $^{12}C_{70}$:$^{12}C_{69}{}^{13}C$ peaks.

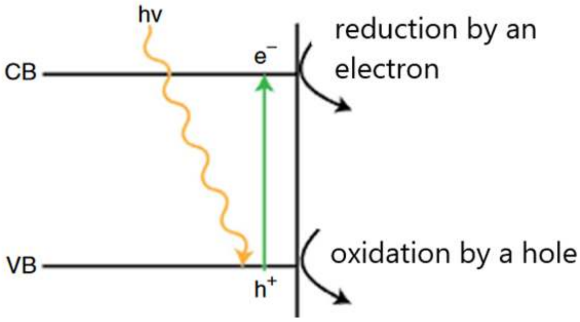
(k) **Determine** the first fullerene for which the peak with one ^{13}C is more abundant than the peak with no ^{13}C.

(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 ($\Delta_rG°_{298}$ = +237 kJ / mol of H_2O), carbon dioxide methanation ($\Delta_rG°_{298}$ = +818 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.

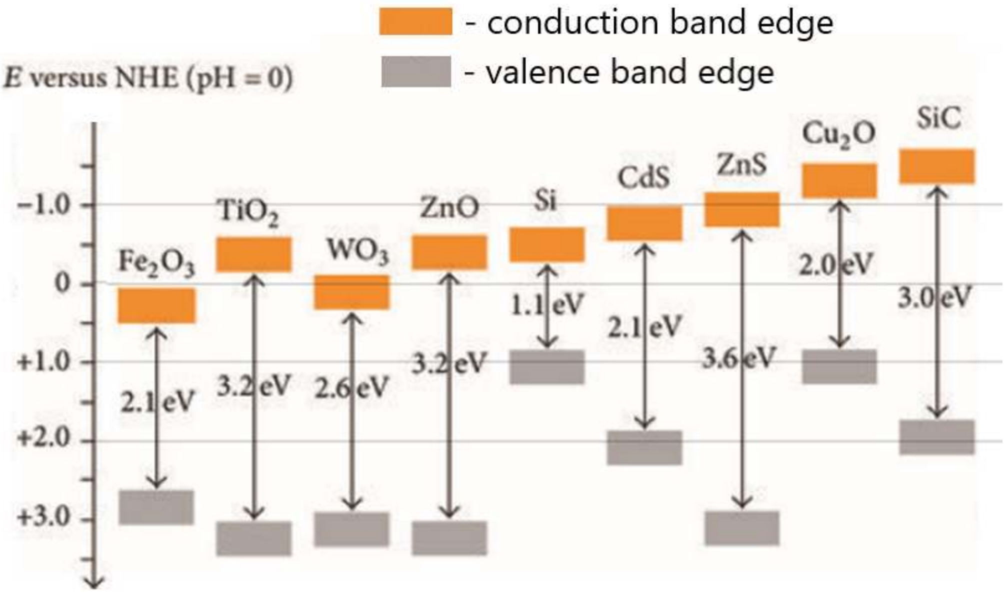
Consider two photochemical reactions: water splitting and carbon dioxide methanation by water. In both reactions consider an acidic medium.

(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)
$O_2 \rightarrow H_2O$	1.23
$CO_2 \rightarrow CH_4$	0.17
$H^+ \rightarrow H_2$	0

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

i) oxidise water to O_2;

ii) reduce water to H_2;

iii) reduce carbon dioxide to methane

iv) both oxidise and reduce water.

The catalytic activity of photocatalysts is evaluated by the normalised reaction rates measured, e.g., in μmol·h^{-1}·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:

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

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):

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

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 μmol·h^{-1}·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:

$$\lambda_{cutoff} = \frac{hc}{E_{\text{g}}}$$

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 2×10^5 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:

$$E_g(R) = E_g^{\infty} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R}$$

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 = 1.602×10^{-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 (aB) 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:

$$\lambda_{cutoff} = \frac{hc}{E_{\mathrm{g}}(R)}$$

(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.
$\Delta_{vap}S^\circ(H_2O)$ = 118 J / (mol·K)
$\Delta_{vap}H^\circ(H_2O)$ = 44 kJ / mol

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

The reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

which accounts for ~20% of global CO_2 emissions, is highly favourable thermodynamically ($\Delta_rG^\circ_{298}$ = –818 kJ / mol) and releases much heat ($\Delta_rH^\circ_{298}$ = –890 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 $\Delta_rG^\circ(T)$ 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 ($\Delta_rG^\circ_{298}$ = –131 kJ / mol; $\Delta_rH^\circ_{298}$ = –253 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:

$$CO_2(g) + 2H_2O(l)$$

$$CH_4(g) + 2O_2(g)$$

$$CO_2(g) + 2H_2(g) + O_2(g)$$

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

$$CO_2(g) + 4H_2(g) \rightleftarrows CH_4(g) + 2H_2O(g)$$

(d) The mixture $CO_2 : H_2 = 1 : 4$ 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 °C
- Freezing point depression constant (K_f) for the solvent: 4.5 $\mathrm{K \cdot kg \cdot mol^{-1}}$
- Standard enthalpy of vaporisation of the solvent: 25.0 $\mathrm{kJ \cdot mol^{-1}}$
- Vapour pressure of the pure solvent at −15 °C : 0.0075 atm
- The freezing point of the solution containing the drug: −16.5 °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 $45\ ^\circ\mathrm{C}$. The temperature of the atmosphere decreases linearly by $6.5\ ^\circ\mathrm{C}$ 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:

$$\frac{P}{T_\mathrm{m} - 273} = -1.34 \cdot 10^4\ \mathrm{kPa\ K^{-1}}$$

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 absense 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 $-6\ ^{\circ}\mathrm{C}$.

Process	**Energy (kJ/mol)**
Sublimation enthalpy of silver ($\Delta_{sub}H^0$(Ag))	+285
Sublimation enthalpy of iodine ($\Delta_{sub}H^0(I_2)$)	+57
Bond dissociation enthalpy of iodine ($\Delta_{diss}H^0(I_2)$)	+150
Ionisation enthalpy of silver ($\Delta_{Ion}H^0$(Ag))	+731
Electron affinity of iodine ($\Delta_{aff}H^0$(I))	-295
Formation enthalpy ($\Delta_f H^0$(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 ($\Delta_{\mathrm{f}} H_{\mathrm{lattice}}$(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:

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

where γ_{iw} is the interfacial tension between ice and water, ΔG_ν 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 $0^\circ C$) 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, $\Delta G_c = 108.3\ \mathrm{kJ}/\mathrm{mol}$ for a degree of supercooling of $10\ ^\circ\mathrm{C}$, whilst $\Delta G_{sl} = -350\ J/\mathrm{mol}$.

(d) **Find** the critical Gibbs free energy change for nucleation of AgI at a degree of supercooling of $6\ ^\circ\mathrm{C}$.

(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.

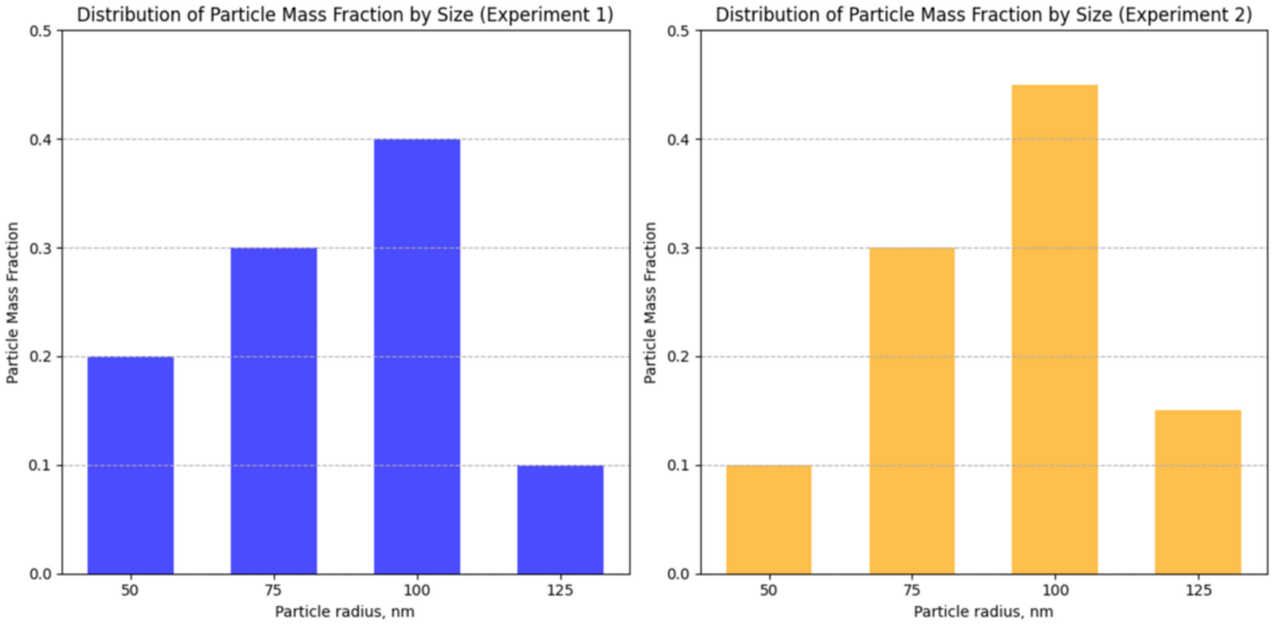
A) above the city

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.

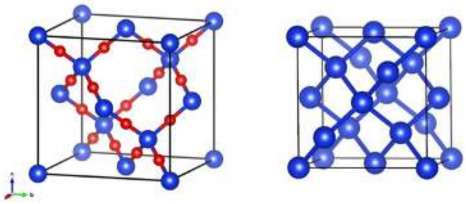
(h) **Check** if the order of the rain precipitation reaction for AgI is 0, 1 or neither.

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.

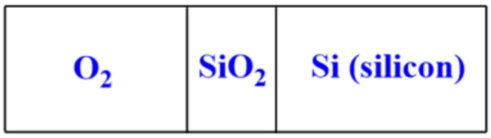
Both SiO_2 and Si have cubic unit cells, as shown below.



The Si unit cell parameter is 5.43 Å and the Si-O bond length is 1.54 Å. Assume that Si-O-Si bond angle is 180^{o}.

(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.



In a 0.5 dm^3 chamber with initial pressure of O_2 of 1.5 bar at 923 ^{o}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 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.

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

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:

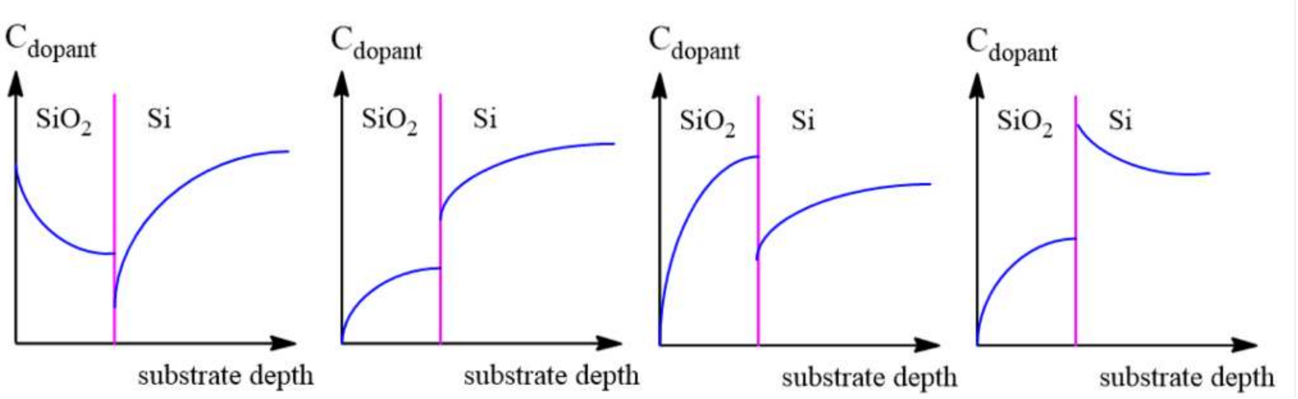
A) n
B) p
C) n+p,
D) neither n nor p

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*:

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

The concentration profile of the dopants across the substrate depends on the value of *K* as well as dopant diffusion in Si and SiO_2.

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/dm^2. At equilibrium at 1200 K, the segregation coefficient, K = 0.70. The total thickness of the Si layer is 300 nm and the SiO$_2$ layer is 100 nm.

(m) **Calculate** the concentrations C_{SiO2} 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.

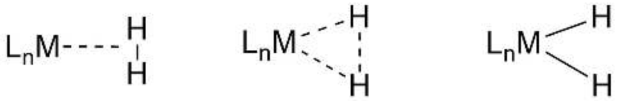
(c) **Order** the following compounds in order of their O-O bond length and **calculate** the O-O bond order for each case: O_2 , KO_2, BaO_2, and $[O_2][Pt^{V}F_6]$.

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.

$W(CO)_5H_2$ $\qquad$ $Ir(PPh_3)_2H_2$

(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:

$W(CO)_5H_2$ $\qquad$ $W(CO)_4(PPh_3)H_2$ $\qquad$ $W(CO)_4(Cl)H_2$

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

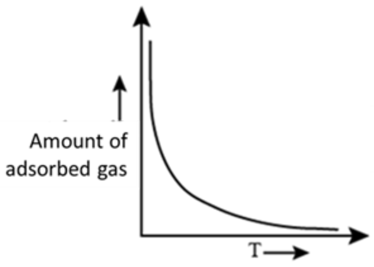
(e) **Arrange** the following complexes in order of decreasing H-H bond distance:

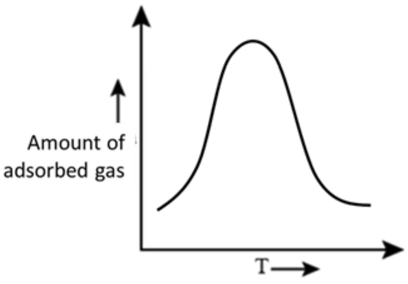
$Ir(CO)_3(F)H_2$ $\qquad$ $Ir(CO)_3(Cl)H_2$ $\qquad$ $Ir(CO)_3(I)H_2$

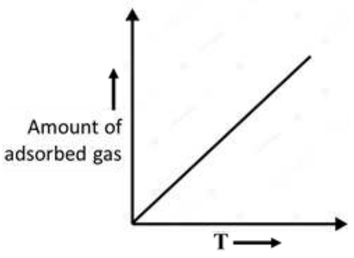
25. Adsorption and heterogeneous catalysis

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.







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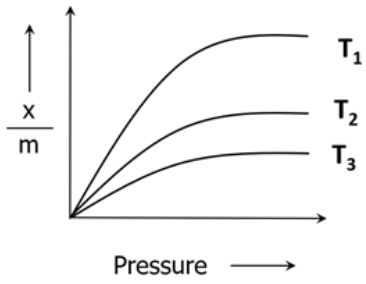
The amounts of physically adsorbed gas per unit mass of adsorbent (x/m) vs. pressure (P) are plotted below for a gas at different temperatures.



(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 0.16×10^{-14} 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.

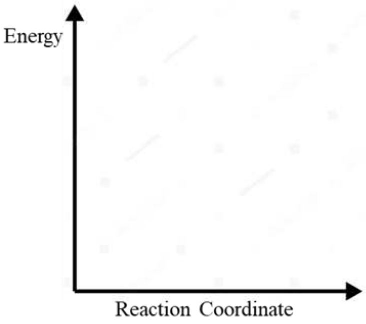
(iv) Nanoparticles are easier to prepare than large particles.

(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 g/mL) was passed through a column packed with 30 g of solid KCl, with a flow rate of about 117 μL/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 ($C_5H_{11}OH$) 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 $M(NH_3)_6^{2+}$	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

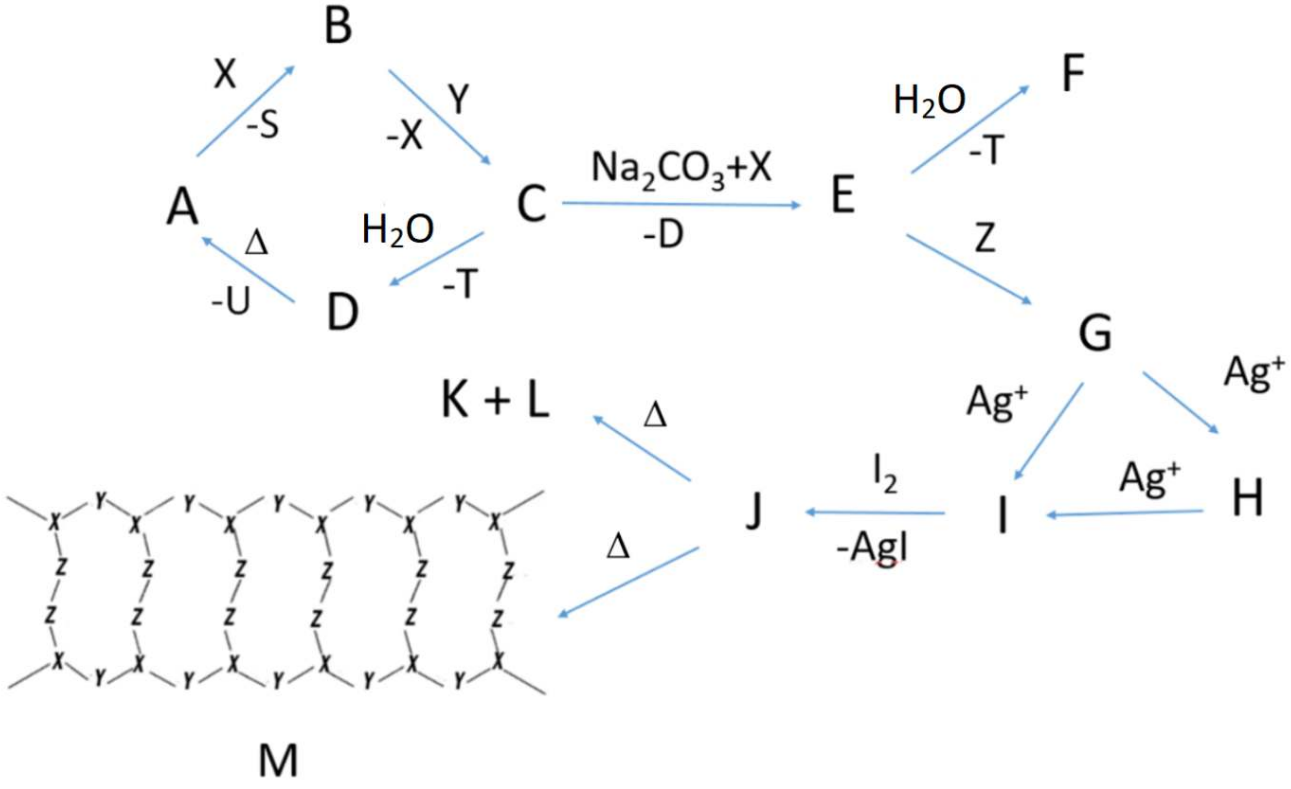
E) M-Cl bond breaking

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-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_2O_7^{2-}$, $S_2O_8^{2-}$, 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 $SO_{2(g)}$ and $SO_{2(aq)}$ 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?

$$K(\text{Henry}) = 1.3\ \text{mol/(L·atm)};\ \text{p}K_{a1}(H_2SO_3) = 1.80 \text{ and } \text{p}K_{a2}(H_2SO_3) = 7.20$$

(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.

$$\text{p}K_{a2}(H_2SO_4) = 2.00$$

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*-quinone/1,2-dihydroxybenzene) = 0.69 V and $E^0(SO_4^{2-}/SO_3^{2-})$ = 0.24 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 RCH(OH)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 $Au_2(SeO_3)_3$, 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 $Au_2(SeO_3)_3$.

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 $Na_2S_2O_3$ 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 CO_2 molecule have?

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

(c) **Does** the spectrum of SO_2 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).

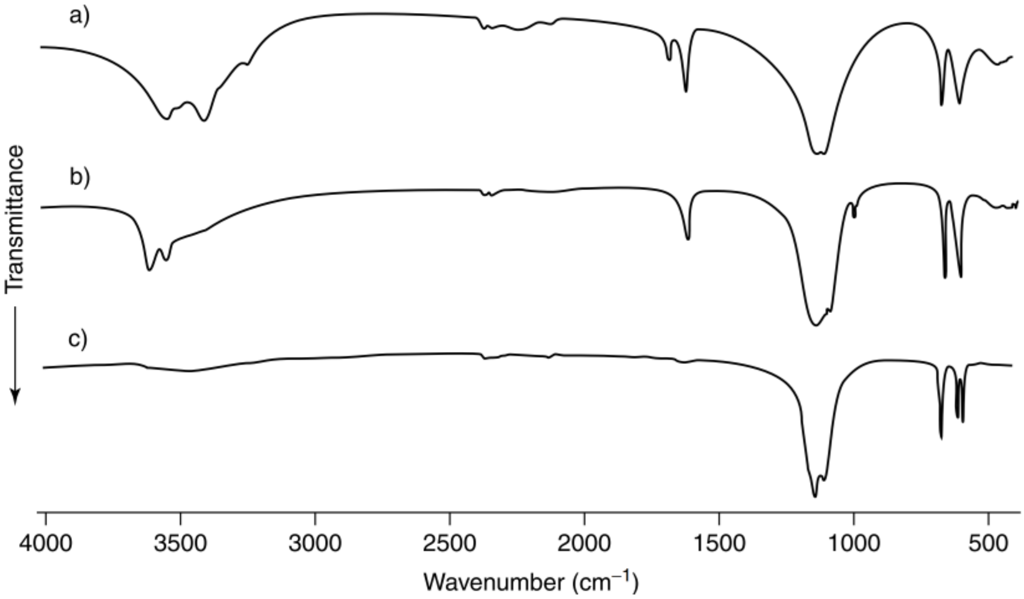
$$\mu^{-1} = m_1^{-1} + m_2^{-1}$$

(d) In the infrared spectrum of SO_2 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.



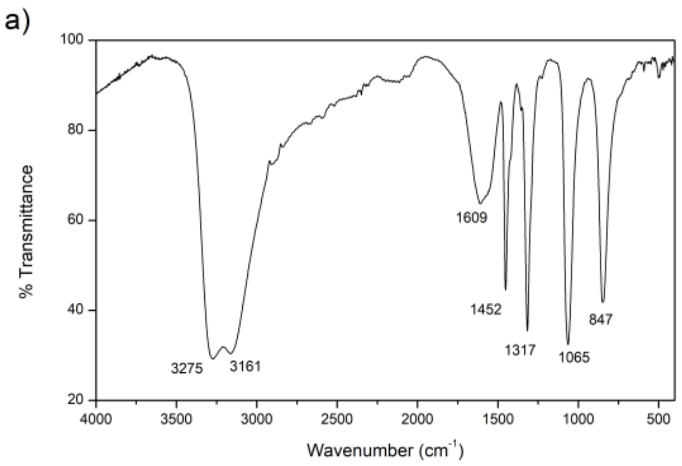
(g) **Is it possible** to distinguish which bands correspond to water and which bands correspond to the sulfate anion? **Determine** the spectrum that corresponds to anhydrite.

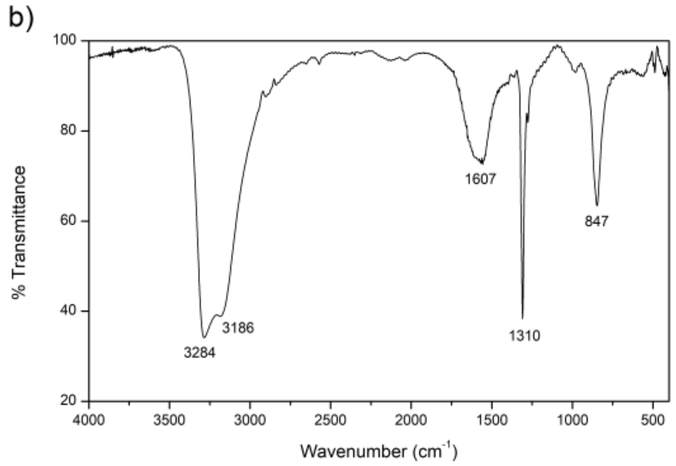
30. Applications of infrared spectroscopy to coordination chemistry

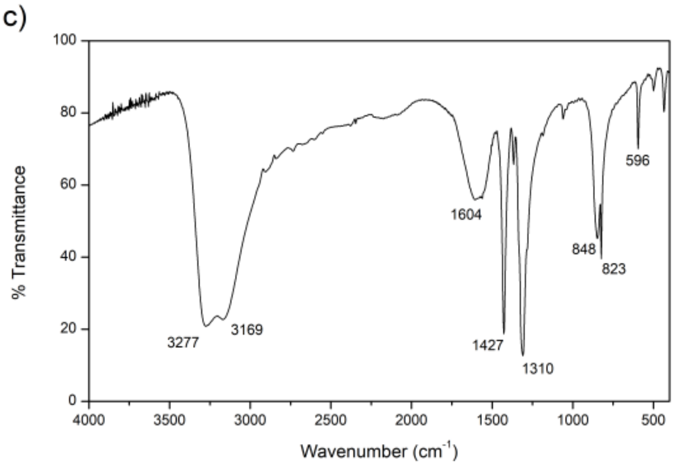
Part A

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 $[Co(NH_3)_5Cl]Cl_2$ with $NaNO_2$ yields two complexes of general formula $[Co(NO_2)(NH_3)_5]Cl_2$. These two complexes differ in the mode of coordination of the NO_2^- anion (nitro: $-NO_2$ and nitrito: $-ONO$). 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, $[M(CO)_6]^{x+}$, 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 $[M(CO)_6]^{x+}$?

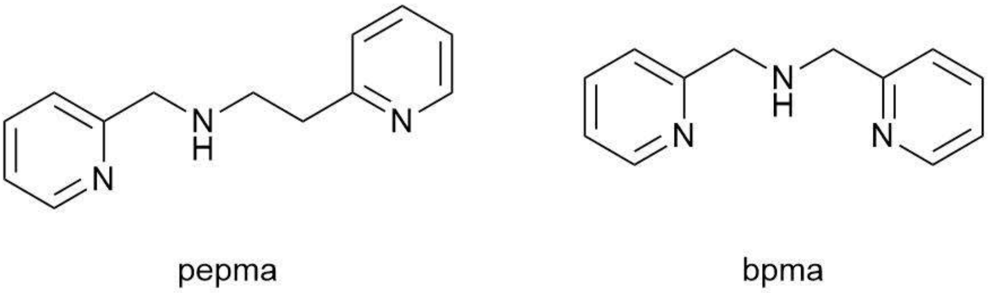
Partial ligand substitution can lead to the formation of complexes such as $[M(CO)_4L_2]^{x+}$, where L is monodentate ligand.

(d) **State** the type and number of possible isomers in complexes of type $[M(CO)_4L_2]^{x+}$.

(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.



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 $\mu \approx 4.0$ 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**.