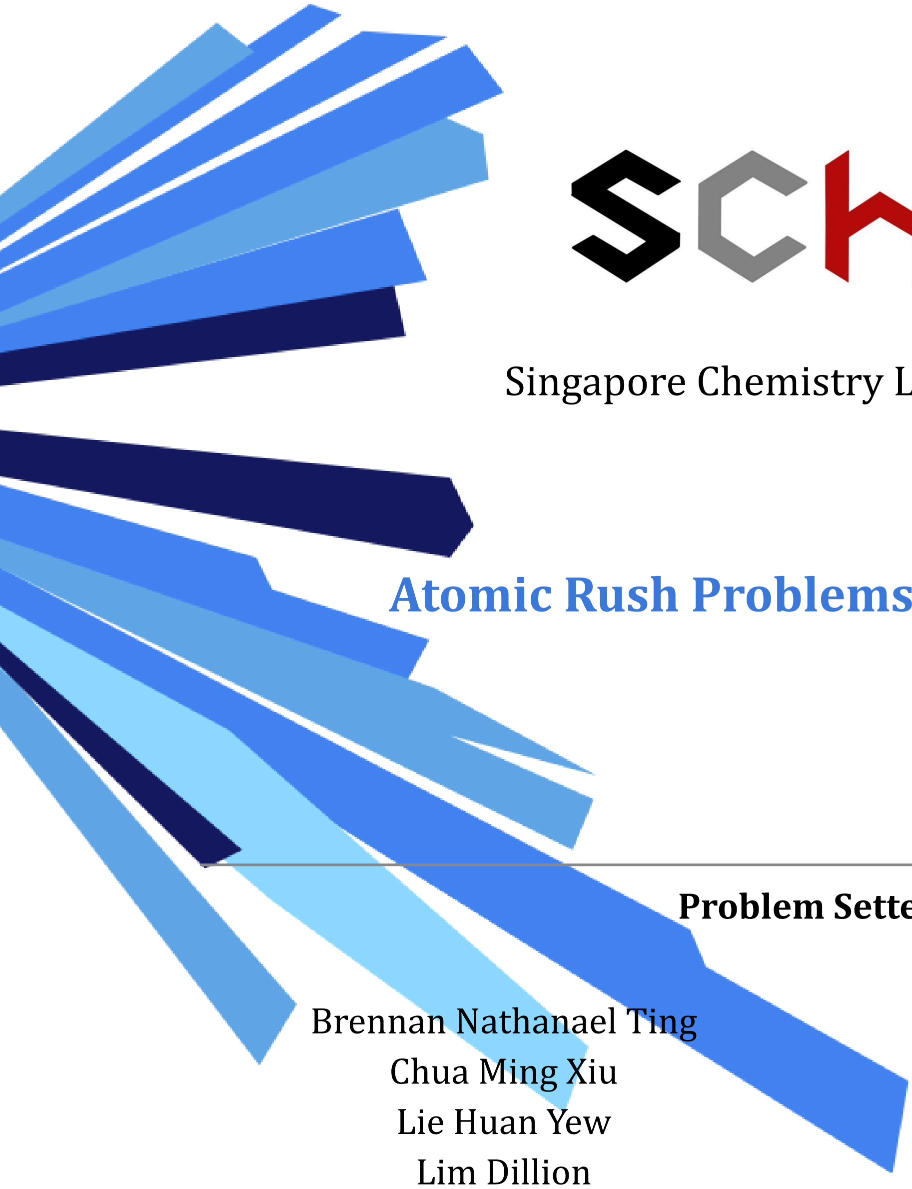

SChL

Singapore Chemistry League 2024

Atomic Rush Problems and Solutions

Problem Setters

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List of Errata

All errata present in the competition duration (as at 100824, from 0900h to 1300h) have been rectified and highlighted in red in the subsequent solutions.

Any dispute of scores owing to the misattribution of points caused by the following errors have been addressed accordingly.

AR9 During the competition duration, the method of input for the final answer of AR9 and AR10 was erroneously swapped. AR9 wrongly prompted a string input when it should be an organic structure input (using a Sketcher tool), while AR10 wrongly prompted an organic structure input when it should be a string input.

Several teams surfaced this issue to the Organising Team, upon which the inputs were swapped back. Meanwhile, many teams had inputted the string equivalent of the correct final answer to AR9 (e.g. ethanal, CH3CHO), but did not receive the allocated points.

However, after the input methods were correctly swapped back, it was found that the Sketcher tool to input the organic structure final answer in AR9 was not functional during the competition. In the interest of fairness for the teams who were not able to answer AR9 after the swap due to this technical issue, this problem has been **voided** from the score tally.

AR10 *See issue to AR9.* AR10 is **not voided** as the correct input method after the swap allowed teams to submit the correct final answer to receive their allocated points.

AR12 Final answer was initially “+1906”. This is wrong as the problem states to leave the final answer to 3 significant figures. The correct final answer is “+1910”.

AR40
AR43
AR50 The Sketcher tool to input the organic structure final answer for these 3 problems was not functional during the competition. These 3 problems are **voided** from the score tally.

The Organising Team takes full responsibility for the above errors.

AR1: Sky High

The Beirut explosion in 2020 was the greatest man-made disaster of recent history — as I am sure most of you have heard of.

Aftermath of the Beirut explosion.[1]

It was caused by the spontaneous ignition of 2750 tonnes of ammonium nitrate via the following reaction:

$$2\ NH_4NO_3\ (s) \rightarrow 2\ N_2\ (g) + O_2\ (g) + 4\ H_2O\ (g)$$

At 260 ^{o}C and atmospheric pressure, what is the total volume of gas produced by the explosion? Assume ideal gas behaviour.

Leave your answer to 3 significant figures, in units of m^3.

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[1] By Mehr News Agency, CC BY 4.0, https://commons.wikimedia.org/w/index.php?curid=92996957

Solution:

5260000

First, we calculate the amount of NH_4NO_3 exploded:

$$M_r(\mathrm{NH_4NO_3}) = 2(14.01) + 4(1.008) + 3(16.00)$$
$$\eta_{\mathrm{NH_4NO_3}} = \frac{2750 \times 10^6}{M_r(\mathrm{NH_4NO_3})}$$

Two moles of NH_4NO_3 produces 7 moles of gas (notice that at ignition temperatures, H_2O is present as a gas), hence the amount of gas produced is $\frac{\frac{7}{2} \times 2750 \times 10^6}{M_r(\mathrm{NH_4NO_3})}$ mol.

Rearranging the ideal gas equation, we obtain:

$$V = \frac{nRT}{p}$$

And substitution of values gives:

$$\begin{aligned} V &= \frac{\frac{\frac{7}{2}\times 2750\times 10^6}{2(14.01)+4(1.008)+3(16.00)} \times 8.3145 \times (260 + 273.15)}{101325} \\ &= 5260100\mathrm{m}^3 \\ &= 5260000\mathrm{m}^3 \ (3 \text{ s.f}) \end{aligned}$$

Problem prepared by: Lin Bohan

AR2: Polysulfanes

Polysulfanes have the general formula H_2S_n, where $n > 1$. They can be considered analogues to alkanes, and exist as oily liquids at room temperature.

H_2S_2 and H_2S_3, the first 2 members of this homologous series.

An 8.00 g mixture containing equal masses of H_2S_n and H_2S_{n+1} is treated with catalytic alkali. The only products are 1.097 dm^3 of a foul-smelling gas (measured at r.t.p) and a yellow solid.

Find the value of *n*.

Solution:

5

The only possible gases that can be produced are H_2 and H_2S (H_2S_2 has a boiling point of 70 °C). Since H_2 is odourless, the gas evolved must be H_2S (characteristic rotten egg smell), and the other product is elemental sulfur. Hence, the general formula for the decomposition of H_2S_n must be:

$$H_2S_n\ (l) \rightarrow H_2S\ (g) + (n-1)\ S\ (s)$$

Amount of H_2S evolved (at r.t.p) $= \frac{pV}{RT} = \frac{1.01325\times10^{5}\times1.097\times10^{-3}}{8.3145\times(20+273.15)} = 0.045603$ mol = sum of amount of H_2S_n and H_2S_{n+1}.

M_r of $H_2S_n = 2.016 + 32.07n$; M_r of $H_2S_{n+1} = 34.086 + 32.07n$

$$\frac{4}{2.016+32.07n} + \frac{4}{34.086+32.07n} = 0.045603$$

$n = 4.95 \approx \mathbf{5}$

Problem prepared by: Wang Jiahua

AR3: Lazier

Lazier's catalyst is sometimes used to refer to copper chromite, a compound often used as a catalyst. Its chemical formula is $Cu_2Cr_2O_5$.

If the oxidation state of Cr is x and the oxidation state of Cu is y, what is the value of $x - y$?

Solution:

1

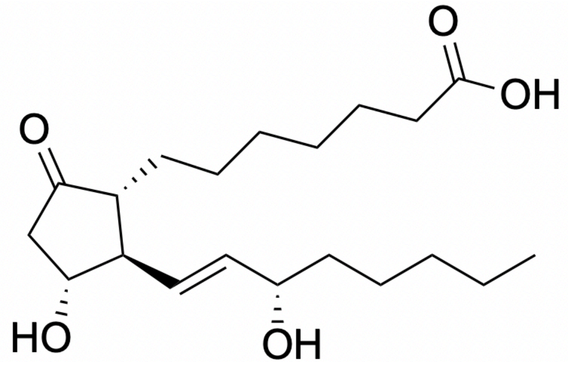
The common oxidation states of Cu are 0, +1 or +2.
If the oxidation state of Cu is 0, then the oxidation state of Cr would be +5, which is rare for Cr.
If the oxidation state of Cu is +1, then the oxidation state of Cr would be +4, which is also rare for Cr.
If the oxidation state of Cu is +2, then the oxidation state of Cr would be +3, which is reasonable.

The difference between their oxidation states is $3 - 2 = \mathbf{1}$.

Problem prepared by: Lim Dillion

AR4: There's More To Prostate Glands Than You Thought

The prostaglandins are a class of small biomolecules who serve a staggering array of critical bioregulatory functions but went unnoticed for a long time. One of the molecules belonging to this family, prostaglandin E1, is shown:

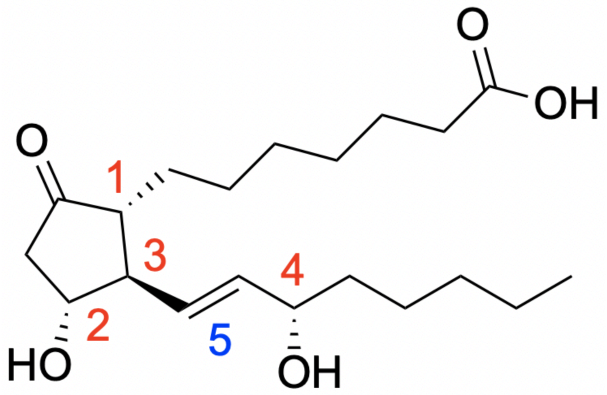


How many stereoisomers, including the one shown, can this molecule have?

Solution:

32

To answer this question we count the number of stereo-elements present. There are 4 chiral centres and 1 double bond, for a total of 5. Using the formula 2^n, where n is the number of stereogenic elements, we have $2^5 = 32$ possible stereoisomers.



Problem prepared by: Lin Bohan

AR5: Curious Carbonate

Compound **A** is a Group 2 carbonate. When 9.867 g of **A** was strongly heated, 7.667 g of solid was left behind. What is the chemical formula for compound **A**?

Leave your answer as a chemical formula. The input is ***case-sensitive****.*

Solution:

$BaCO_3$

$$\begin{aligned}
\eta_{\mathrm{CO_2}} &= \frac{9.867 - 7.667}{12 + 16 \times 2} = 0.0500 \text{ mol} \\
\eta_{\mathrm{MCO_3}} &= \eta_{\mathrm{CO_2}} = 0.0500 \text{ mol} \\
M_r(\mathbf{A}) &= \frac{9.867}{0.0500} = 197.3 \\
A_r(\mathbf{M}) &= 197.3 - (12 + 16 \times 3) = 137.3
\end{aligned}$$

Looking up the periodic table, **M** must be Ba. So, **A** must be $BaCO_3$.

Problem prepared by: Lim Dillion

AR6: Make 'Im Salty

The detection limit for NaCl has been found[2] to be as low as 6.7×10^{-3} mol dm^{-3}.

Deeleon decides to prank his friend Teamotty and prepares a 100 ml solution of NaCl (aq) to pass off as tap water. To ensure Teamotty is assailed by saltiness, he decides to prepare a sample at a concentration of 15 times the above detection limit. What mass of NaCl (s), in grams, should he use?

Leave your answer to 2 significant figures.

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[2] Brosvic, G. M., and W. W. McLaughlin. "Quality Specific Differences in Human Taste Detection Thresholds as a Function of Stimulus Volume." *Physiology & Behavior,* vol. 45, no. 1, Jan. 1989, pp. 15–20. PubMed, https://doi.org/10.1016/0031-9384(89)90160-1.

Solution:

0.59

15 times the concentration of the detection limit corresponds to $6.7 \times 10^{-3} \times 15 = 0.1005\,\text{mol}\,\text{dm}^{-3}$.

To prepare a 100 ml sample at this concentration, 0.1005 mol dm^{-3} × 0.1 dm^{-3} = 0.01005 mol of NaCl is needed (since 1000 mL = 1 dm^{3}), which is $0.01005 \times (22.99 + 35.45) = 0.587\,\text{g}$.

Problem prepared by: Lin Bohan

AR7: Single Bonds Rule Chemistry

The double bond rule states that elements in period 3 and beyond tend not to form double or triple bonds with other elements or itself.

Which of the following simple covalent compound(s) **directly violate** the double bond rule? Assume that octet configuration is fulfilled in all compounds.

A) P_2
B) Li_2
C) BrF
D) SiP^-

Leave your answer as a concatenated string of ***capital letters*** *in ascending alphabetical order. For example, if you believe A, B and D directly violate the double bond rule, leave your answer as "ABD".*

Solution:

AD

A) P_2

P has valence electrons in the 3p subshell, and P_2 contains a triple bond, so the rule is violated.

B) Li_2

Li does not contain valence electrons in subshells of n > 2, so the rule is obeyed.

C) BrF

To fulfil the octet configuration, BrF only contains a single bond, so the rule is obeyed.

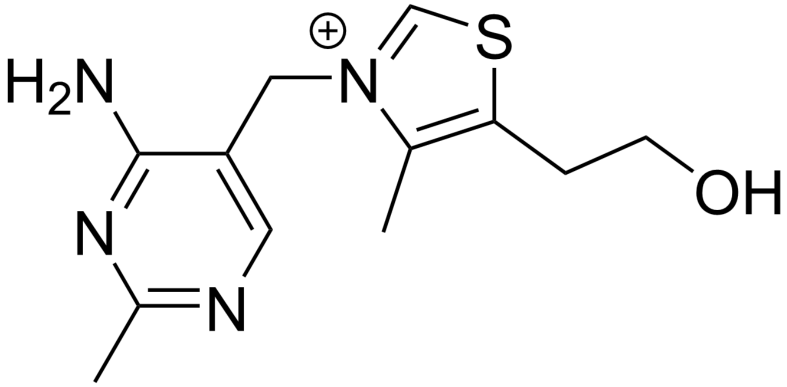
D) SiP^-

Si and P contain valence electrons in the 3p subshell, and to fulfil the octet configuration SiP^- needs to have a triple bond, so the rule is violated.

Problem prepared by: Chua Ming Xiu

AR8: Electrons Of Thiamine

Under physiological conditions, thiamine (Vitamin B1) is present as a cation.



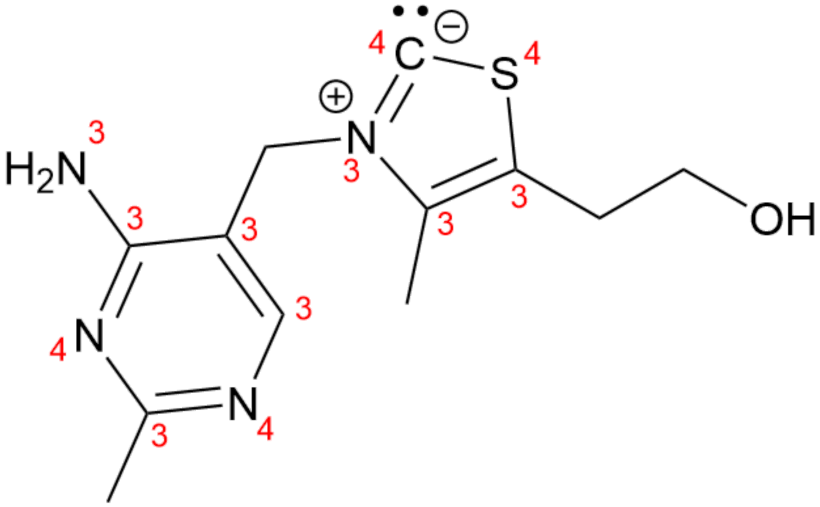
The carbon between the nitrogen and sulfur in the thiazole ring may lose its weakly acidic hydrogen to form what is called an ylide. The negative formal charge on the carbon is stabilised by the positive charge on the adjacent nitrogen.

The ylide of thiamine pyrophosphate, a biological derivative, is a cofactor in pyruvate decarboxylation, the intermediate step between glycolysis and the Krebs cycle in aerobic respiration.

In the thiamine ylide, what is the **total** number of electrons residing in or originating from sp^2 hybrid orbitals? Assume the NH_2 group is planar.

Solution:

40



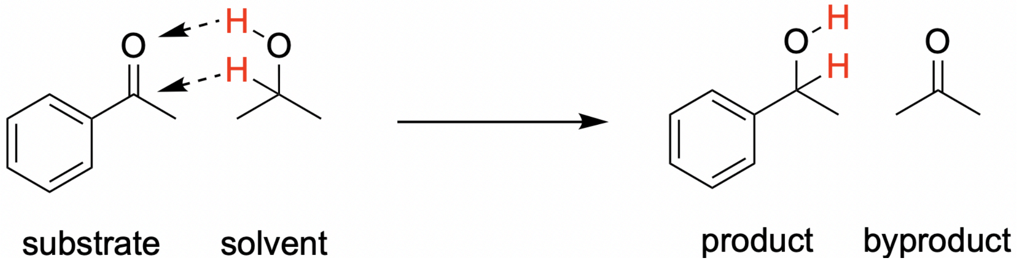
The sulfur atom is sp^2 hybridised. It has three sp^2 hybrid orbitals, two of which are used in σ-bonding with adjacent atoms and contain one electron each, while the last sp^2 hybrid orbital contains a lone pair. The lone pair in its 3p orbital is delocalised in the π-electron cloud of the 5-membered ring, allowing the ring to achieve aromaticity with 6 π electrons.

(In reality, the NH_2 group bonded to the pyrimidine ring is not planar. The N atom is somewhere *between* sp^2 and sp^3 hybridised.)

Problem prepared by: Wang Jiahua

AR9: When Does MPV *Not* Stand For Multi-Purpose Vehicle?

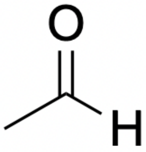
The Meerwein-Ponndorf-Verley (MPV) reduction results in the net reduction of a carbonyl to alcohol, by transferring 2 hydrogens from an existing alcohol (usually the solvent) to the substrate. For example, when $(CH_3)_2CHOH$ (a.k.a. *i*-PrOH) is used as solvent, a schematic interpretation of the reaction is shown:



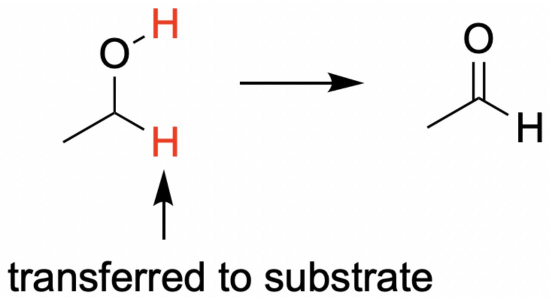
What is the byproduct formed when ethanol is used as solvent?

Leave your answer as an organic structure.

Solution:



The alcoholic solvent essentially loses two hydrogens to convert the alcohol to the corresponding carbonyl compound, i.e:



The corresponding carbonyl compound of ethanol is ethanal (acetaldehyde).

Problem prepared by: Lin Bohan

AR10: When Does MPV *Actually* Stand For Multi-Purpose Vehicle?

Sodium azide, NaN_3 is a chemical that was previously used in car airbags. When a vehicle crashes, NaN_3 is denoted in the reaction shown below:

$$2\ NaN_3\ (s) \rightarrow 2\ Na\ (s) + 3\ N_2\ (g)$$

However, NaN_3 is toxic, so two alternative chemicals have been proposed:

- Nitroguanidine, $(NH_2)_2CNNO_2$. It decomposes according to the equation below:

$$(NH_2)_2CNNO_2\ (s) \rightarrow 2\ H_2O\ (g) + 2\ N_2\ (g) + C\ (s)$$

- Guanidine nitrate, $[C(NH_2)_3]NO_3$. It decomposes according to the equation below:

$$[C(NH_2)_3]NO_3\ (s) \rightarrow 3\ H_2O\ (g) + 2\ N_2\ (g) + C\ (s)$$

If equal masses of each chemical is detonated, assuming the reaction proceeds to completion with 100% yield, arrange the chemicals in descending order, based on the volume of gas they generate when detonated.

A) Sodium azide, NaN_3
B) Nitroguanidine, $(NH_2)_2CNNO_2$
C) Guanidine nitrate, $[C(NH_2)_3]NO_3$

Leave your answer as a concatenated string of ***capital letters****. For example, if you believe A has the largest volume generated, followed by B then C, leave your answer as ABC.*

Solution:

CBA

By Avogadro's law, the volume of gas is directly proportional to the number of moles of gas formed. The number of moles of each chemical is inversely proportional to the molar mass of the chemical, and the number of moles of gas formed is also directly proportional to the mole ratio given by the decomposition equations. So we shall compute two values: the molar mass of each chemical, and the mole ratio of gases formed to explosive.

Sodium azide, NaN_3: $M_r = 65$, Mole ratio = 1.5

Nitroguanidine, $(NH_2)_2CNNO_2$: $M_r = 104$, Mole ratio = 4 (Remember that H_2O will be a gas when exploded)

Guanidine nitrate, $[C(NH_2)_3]NO_3$: $M_r = 122$, Mole ratio = 5

Now, the chemical with the largest value of mole ratio divided by M_r will be the chemical that generates the largest volume of gas. We shall do the computation below:

Sodium azide, NaN_3: $1.5 \div 65 = 0.0231$

Nitroguanidine, $(NH_2)_2CNNO_2$: $4 \div 104 = 0.0385$

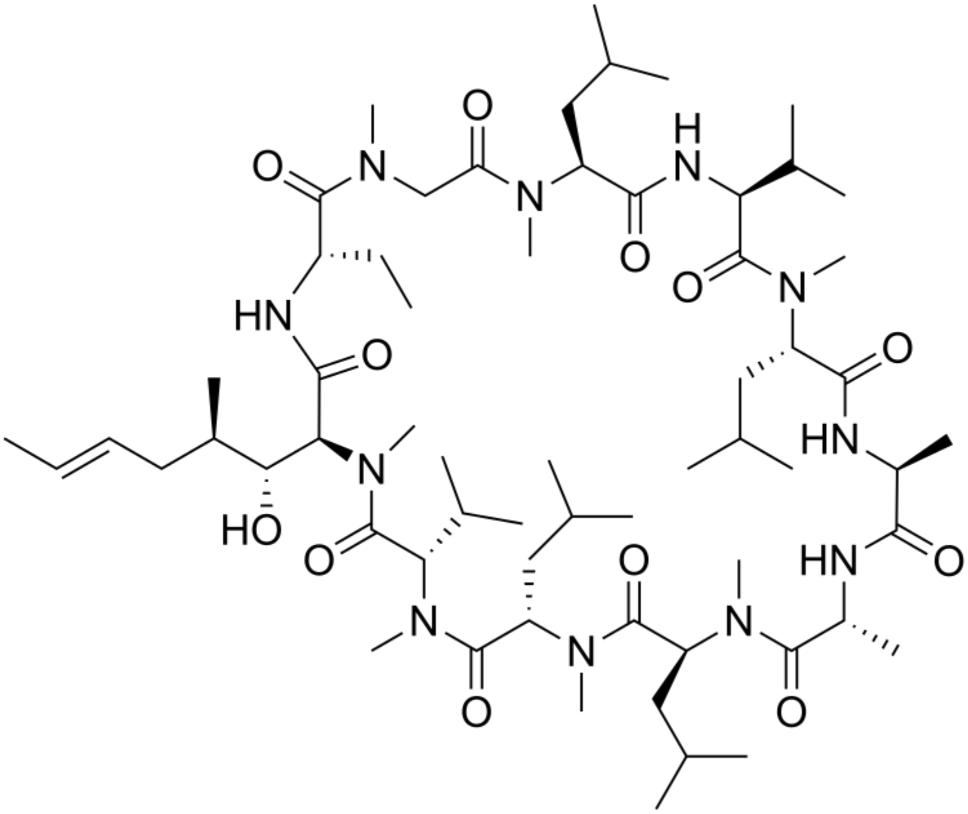
Guanidine nitrate, $[C(NH_2)_3]NO_3$: $5 \div 122 = 0.0410$

Comparing the values, the answer is **CBA**.

Problem prepared by: Lim Dillion

AR11: Cyclo-Peptide

Cyclosporin is a drug that inhibits the function of white blood cells in the body. Thanks to its immunosuppressive properties, it is commonly administered to patients undergoing organ transplants to reduce the chances of tissue rejection.



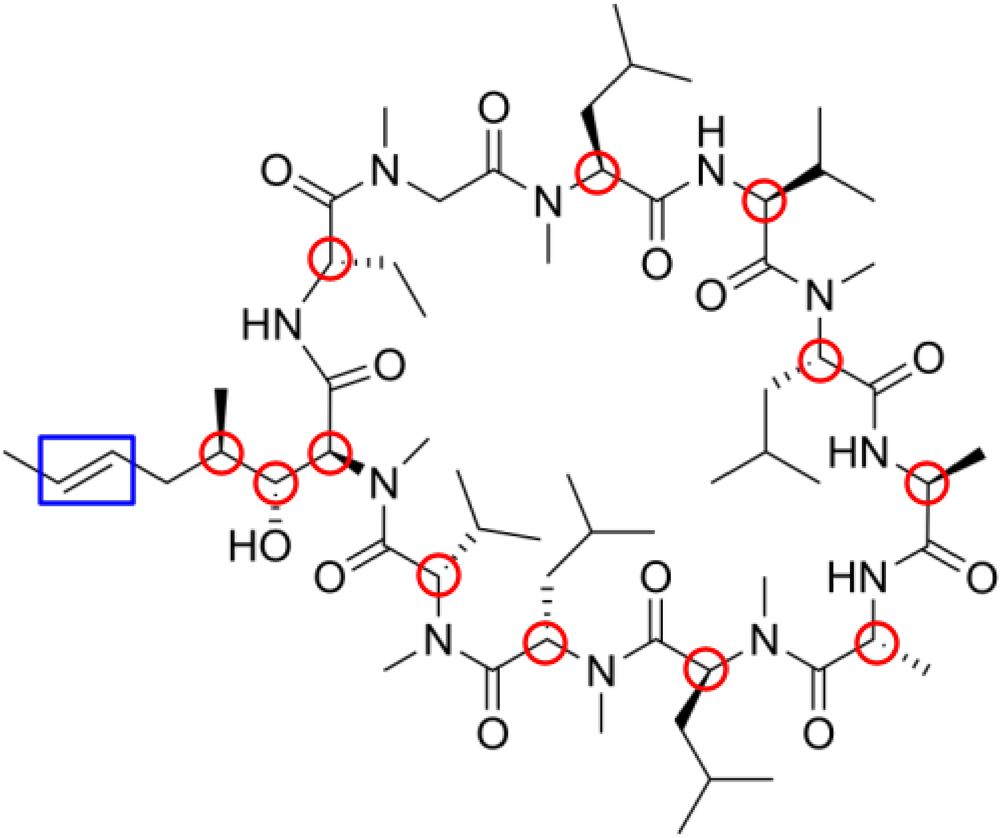
How many stereoisomers does cyclosporin have, including the stereoisomer shown above?

Solution:

8192

Recall that the number of stereoisomers a compound has = 2^n, where n = number of chiral centres + number of stereogenic alkene groups.

The chiral centres are circled in red, while the stereogenic alkenes are boxed in blue.



Note that the amide nitrogen atoms cannot be considered chiral centres, despite seemingly having 4 distinct groups around them (1 carbonyl, 2 R groups and 1 lone pair). This is because the lone pair is delocalised into the carbonyl, causing the N−C=O group to form a conjugated π system that is sp^2 hybridised. Hence the geometry around the N atom is trigonal planar, which contradicts the tetrahedral geometry required for chirality.

There are 12 chiral centres and 1 stereogenic alkene (that can exist as E/Z conformers).

Hence the molecule can have $2^{12+1} = 2^{13} = 8192$ different unique stereoisomers.

Problem prepared by: George Zhou

AR12: Reaction Enthalpies

Calculate the enthalpy change of the following reaction, in kJ mol^{-1}, making use of the values below.

$$2H_2O\ (l) \rightarrow O_2\ (g) + 4\ H^+\ (aq) + 4\ e^-$$

BE (O−H)	+460 kJ mol^{-1}
BE (O=O)	+496 kJ mol^{-1}
$\Delta H_{vap}(H_2O\ (l))$	+41 kJ mol^{-1}
1st IE of H	+1310 kJ mol^{-1}
$\Delta H_{hyd}(H^+)$	−1190 kJ mol^{-1}

Leave your answer to 3 significant figures. Include a "+" or "−" sign.

Solution:

+1910 (not +1906)

To solve this problem, we can construct an energy cycle, since we know the enthalpy changes of each component reaction:

$$H_2O\ (l) \rightarrow H_2O\ (g) \qquad \mathbf{\Delta H_1} = \Delta H_{vap}(H_2O\ (l)) = +41\ \text{kJ mol}^{-1}$$

$$H_2O\ (g) \rightarrow 2H\ (g) + \frac{1}{2}O_2\ (g) \qquad \mathbf{\Delta H_2} = 2BE(O–H) - \frac{1}{2}BE(O{=}O) = +672\ \text{kJ mol}^{-1}$$

$$H\ (g) \rightarrow H^+\ (g) + e^-\ (g) \qquad \mathbf{\Delta H_3} = 1^{st}\ \text{IE of H} = +1310\ \text{kJ mol}^{-1}$$

$$H^+\ (g) \rightarrow H^+\ (aq) \qquad \mathbf{\Delta H_4} = \Delta H_{hyd}(H^+) = -1190\ \text{kJ mol}^{-1}$$

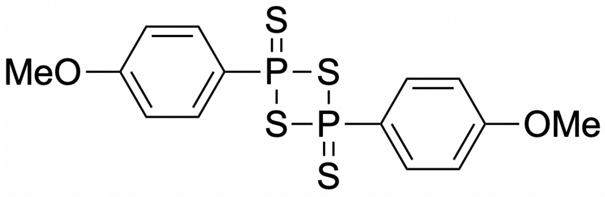
$$\begin{tikzcd}
2H_2O\ (l) \arrow[r, "\mathbf{\Delta H_r}"] \arrow[d, "2\Delta H_1"'] & O_2\ (g) + 4H^+\ (aq) + 4e^- \\
2H_2O\ (g) \arrow[d, "2\Delta H_2"'] & \\
4H\ (g) + O_2\ (g) \arrow[r, "4\Delta H_3"] & 4H^+\ (g) + O_2\ (g) + 4e^- \arrow[uu, "4\Delta H_4"']
\end{tikzcd}$$

$$\begin{aligned}
\Longrightarrow \Delta H_r &= 2\Delta H_1 + 2\Delta H_2 + 4\Delta H_3 + 4\Delta H_4 \\
&= 2(+41) + 2[2(+460) - 12(496)] + 4(+1310) + 4(-1190) \\
&= +1906\ \text{kJ mol}^{-1}
\end{aligned}$$

Problem prepared by: George Zhou

AR13: Lawl Son

Lawesson's reagent is a thiolating agent used in organic synthesis:



Assuming idealised geometry around the phosphorus atoms and assuming the 4-membered ring is planar, what is the P–S–P bond angle in degrees?

Leave your answer to 1 decimal place.

Solution:

70.5

The central P–S–P–S ring forms a rhombus. The P atom has 4 regions of electron density and no lone pairs, hence has tetrahedral geometry.

The S–P–S bond angle would be 109.5° assuming idealised bond angles (more precisely 109.47°, but this does not affect the final answer). Hence, the P-S-P bond angle is 180° – 109.5° = **70.5**°.

Problem prepared by: Lin Bohan

AR14: Iron't You Glad For Steel

When finely divided iron burns in air, it reacts with oxygen gas to form iron oxide, under the following reaction:

$$4\ Fe\ (s) + 3\ O_2 \rightarrow 2\ Fe_2O_3\ (s)$$

This reaction incorporates oxygen atoms into the iron, which is why the mass of iron seems to increase throughout its combustion, as opposed to decreasing as we would typically expect when we burn a piece of wood or paper.

A 20.0 g piece of steel wool, made of 95% iron by mass, is allowed to burn in excess oxygen. Assuming only the iron content in the wool reacts, calculate the final mass of the wool, in grams, when combustion is complete.

Leave your answer to 3 significant figures.

Solution:

28.2

For a 20.0 g piece of steel wool that is 95% iron by mass,

$$\begin{aligned}\text{Mass of iron component} &= 19.0\text{ g}\\ \text{Mass of non-iron component} &= 1.0\text{ g}\end{aligned}$$

$$\text{Amount of iron present} = \frac{19.0}{55.85} = 0.34020\text{ mol (5 s.f.)}$$

4 mol iron reacts to form 2 mol Fe_2O_3.

$$\begin{aligned}\text{Amount of } Fe_2O_3 \text{ formed} &= 0.3402042 = 0.17010\text{ mol}\\ \text{Mass of } Fe_2O_3 &= 0.17010[2(55.85) + 3(16.00)] = 27.16497\text{ g}\end{aligned}$$

$$\begin{aligned}\Longrightarrow \text{Final mass of wool} &= \text{mass of } Fe_2O_3 + \text{mass of non-iron component}\\ &= 27.16497 + 1.0\\ &= 28.2\text{ g (3 s.f.)}\end{aligned}$$

Problem prepared by: George Zhou

AR15: Gus' Gases

Clumsy Gus, having mislabelled five containers in the laboratory, has enlisted your assistance in fixing this problem. You are tasked with identifying the gases in containers V to Z and matching them with their identities 1 to 5.

Gus has only the following information regarding the gases in the containers:

least easily liquefied $\longrightarrow$ most easily liquefied

V **Y** **X** **Z** **W**

The identity of the gases are as follows:

no.	**1**	**2**	**3**	**4**	**5**
gas identity	Kr	HF	CH_4	BrCl	H_2O

Match the gases' identities to their containers.

*Leave your answer as a concatenated string of alternating capital letters and numbers in alphabetical order. For instance, if you believe **V** matches to **1**, **W** to **2**, **X** to **3** and so on, input V1W2X3Y4Z5.*

Hint: the higher the boiling point, the easier it is to liquefy.

Solution:

V3W5X4Y1Z2

How easily a gas is liquefied depends on the strength of the intermolecular forces of attraction (IMF) between atoms/molecules in that gas — the stronger the IMF, the easier it is for the gas to be liquefied. In fact, liquefying is the reverse process of boiling, so we can simply check the boiling point of each gas, rank them in order of increasing boiling point, and match them in order to the letters given.

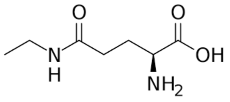
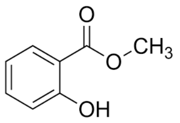
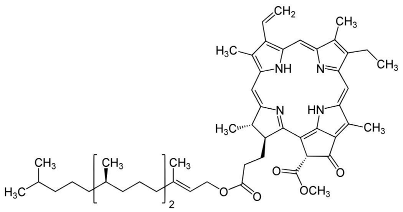
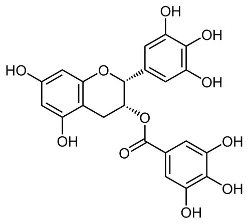
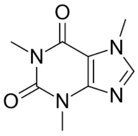
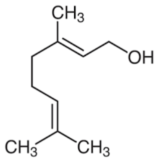
no.	**1**	**2**	**3**	**4**	**5**
gas identity	Kr	HF	CH_4	BrCl	H_2O
b.p. / °C	–153.4	19.5	–161.5	5	100

In greater detail, we note that of the five gases, HF and H_2O have the strongest IMF (hydrogen bonds) between their molecules; H_2O forms more extensive hydrogen bonds than HF since each molecule can form two hydrogen bonds compared to only one in HF. **W** therefore corresponds to H_2O and **Z** to HF. BrCl has a permanent dipole whereas Kr and CH_4 do not, hence it has the strongest IMF of the three and corresponds to **X**. The strength of dispersion forces increases with a larger electron cloud; since Kr has 36 electrons while CH_4 only has 10, Kr has the stronger IMF and corresponds to **Y**, whereas CH_4 corresponds to **V**.

Problem prepared by: Lie Huan Yew

AR16: Bri'ish???

Let us have a bit of fun! Match the following compounds to their tastes / effects in tea!

S/N	Compounds	Function / Effect
1	 (A)	Gives tea its bitter taste
2	 (B)	Makes you stay awake after drinking tea
3	 (C)	Gives tea its sweet and umami taste, and promotes relaxation
4	 (D)	Gives tea its dark colour
5	 (E)	Gives tea its floral aroma
6	 (F)	Gives tea its fruity aroma

Match the functions to the correct compound in each row. If the function in row 6 matches compound A, function in row 5 matches compound B and so on, leave your answer as 654321.

Leave your answer as a 6 digit number.

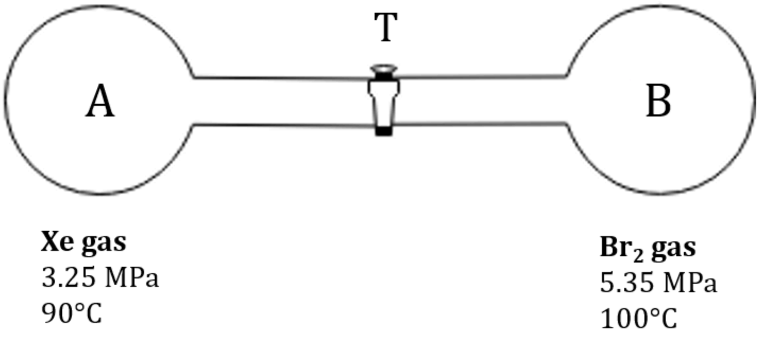
Solution:

364125

Compound A is an amino acid, giving it the sweetness.
Compound B is methyl salicylate, giving it a fruity smell associated with esters.
Compound C is a pheophytin, a dark coloured pigment.
Compound D is a polyphenol, giving tea its bitter taste.
Compound E is caffeine, making you stay awake.
Compound F is geraniol, giving tea its floral smell.

Problem prepared by: Lim Dillion

AR17: Two Containers



Two extremely large containers, **A** and **B** are separated by an extremely thin tube with a tap **T** between them. When tap **T** is opened, gases can freely flow between both containers. Containers **A** and **B** contain gases, at the respective pressures and temperatures above.

Suppose tap **T** was opened, and the temperature of the whole system was adjusted to 25 °C. Given that container **A** had a volume half that of container **B**, calculate the **final** pressure of the system, in megapascals (MPa).

Leave your answer to 2 significant figures.

Solution:

0.89

The number of moles initially in the system is given as the sum of the number of moles of gas in **A** and **B**. However, at 25°C, bromine condenses into a liquid (Br_2 has a boiling point of 58.8°C at atmospheric pressure. Notice that boiling point increases with increasing pressure by the Clausius-Clapeyron equation, so the boiling point at megapascals of pressure will definitely be higher than 25°C). Hence, the final number of moles in the system is the number of moles of gas initially present in container **A**.

After the tap was opened, the volume that the Xe gas can occupy is 3 times larger than the initial volume. Letting the initial volume of container **A** be V, we can let the volume of container **B** be $2V$. So, the total volume after the tap was opened is $3V$.

Now, by the ideal gas law,

$$\eta_{\mathrm{Xe}} = \frac{pV}{RT} = \frac{3.25 \times 10^6 \times V}{8.3145 \times (90 + 273.15)}$$

$$P_{\mathrm{Final}} = \frac{\eta_{\mathrm{Xe}} RT}{V} = \frac{\frac{3.25 \times 10^6 \times V}{8.3145 \times (90 + 273.15)} \times 8.3145 \times (25 + 273.15)}{3V} = \boxed{889428 \text{ Pa}}$$

Hence, the final pressure is 889428 Pa (to 6 s.f.), which is **0.89** MPa (to 3 s.f.).

Problem prepared by: Lim Dillion

AR18: A Feisty Redox Reaction

The synthesis of azides (N_3^-) takes place via the following simplified equation:

$$3\ NH_2^- + NO_3^- \rightarrow N_3^- + 3OH^- + NH_3$$

How many different oxidation states for nitrogen are there in this equation? For N_3^-, use the average oxidation state of nitrogen.

Solution:

3

The corresponding oxidation states of each nitrogen-containing species is shown below:

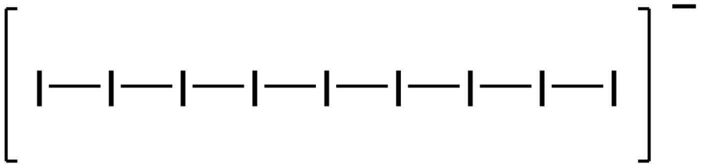
$$3\,\underset{-3}{\mathrm{N}}\mathrm{H_2^-} + \underset{+5}{\mathrm{N}}\mathrm{O_3^-} \rightarrow \underset{-\frac{1}{3}}{\mathrm{N_3^-}} + 3\mathrm{OH^-} + \underset{-3}{\mathrm{N}}\mathrm{H_3}$$

Problem prepared by: Lin Bohan

AR19: Iodiodio…diodiodide

One of the most interesting features of iodine is its ability to form polyatomic anions with itself. These ions have the general formula $[I_n]^{m-}$, where n ranges from 3 to 29, or can even be infinity (in the case of an infinite polymer that was reported in 2016).

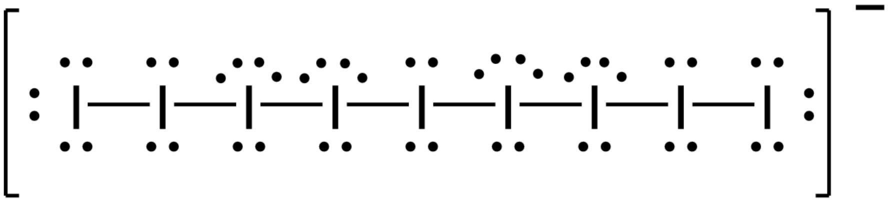
The $[I_9]^-$ ion is found in the compound $(CH_3)_4NI_9$. The shape of polyiodide ions depends on the cation, but here we assume that it is a distinct linear molecule with constant I—I bond lengths.



How many **different** ways are there to distribute the valence electrons among the iodine atoms in $[I_9]^-$, such that

- All atoms have formal charges of either −1, 0, or +1, and
- All electrons are paired?

Here is one possible arrangement:



Solution:

19

The ion has a total of $9 \times 7 + 1 = 64$ electrons. 16 are already present in the single bonds, so we have to add 48 more (in 24 pairs).

The two terminal atoms must have 3 lone pairs to achieve a formal charge of 0 (1 more or 1 less pair will result in a FC of -2 or $+2$ respectively). Among the seven remaining atoms, four atoms will have 3 lone pairs (FC $= -1$) while three atoms will have 2 lone pairs (FC $= +1$). The overall charge of the ion is $4(-1) + 3(1) = -1$.

There are a total of 3 symmetrical arrangements (including the example given).

0	+1	−1	−1	+1	−1	−1	+1	0
0	−1	+1	−1	+1	−1	+1	−1	0
0	−1	−1	+1	+1	+1	−1	−1	0

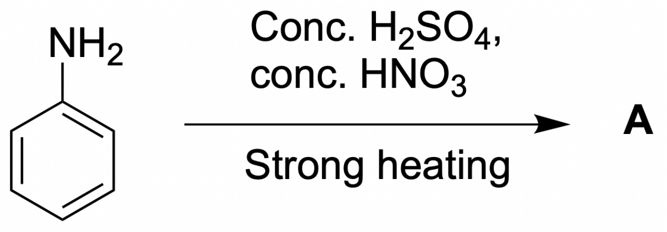
How about the number of unsymmetrical arrangements? The number of ways to arrange 7 objects in a row, in which 4 are of the same type and 3 are of a different type, is $\frac{7!}{4!\times3!} = 35$. Subtracting the 3 symmetrical arrangements, there are 32 unsymmetrical ones. However, there are only $\frac{32}{2} = 16$ **different** arrangements, because when we rotate the ion by 180 degrees the arrangement stays, which means each unsymmetrical arrangement is counted **twice**.

These 2 are the same	0	+1	−1	+1	−1	−1	+1	−1	0
	0	−1	+1	−1	−1	+1	−1	+1	0

Hence the total number of different arrangements is $16 + 3 =$ **19**.

Problem prepared by: Wang Jiahua

AR20: A Simple Nitration



Product **A** is a mixture of 3 products of this nitration of aniline, and has a single nitro (–NO_2) group substituted for each product. Denoting the original –NH_2 group as the 1 position (as shown above), which position has the least substitution occuring?

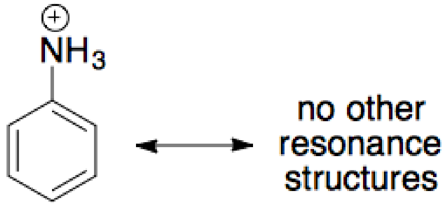
Note: Since this molecule is symmetrical, **leave your position between 2 and 4**. Position 6 is equivalent to position 2, and position 5 is equivalent to position 3.

Leave your answer as either '2', '3' or '4'.

Solution:

2

When concentrated H_2SO_4 and HNO_3 is added, the aniline is first protonated. Now, we get the anilinium cation, which has no resonance structures (no, it is not meta-directing, try drawing out the cation)!



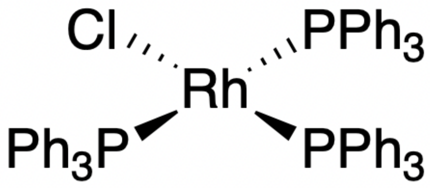
Therefore, we need to consider inductive effects. Since inductive effects get weaker with increasing distance, the *ortho* (2) position has the lowest electron density since $–NH_3^+$ is a very strong electron-withdrawing group. It is therefore least formed. Thus, the answer is **2.**

Problem prepared by: Lim Dillion

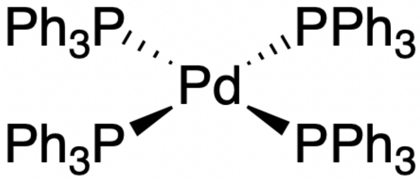
AR21: Feeling Flat

Square planar complexes are generally favoured over tetrahedral complexes by d^8 metals in low-spin environments, thanks to crystal field stabilisation effects.

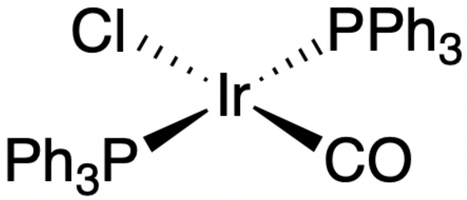
One of the following is an imposter masquerading as a square planar complex when it is in fact tetrahedral — can you spot which one it is?



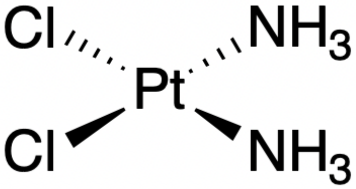
1



2



3



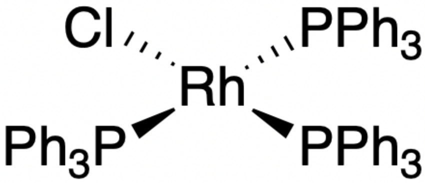
4

Solution:

2

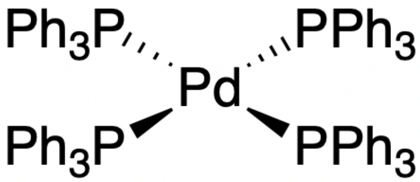
All of the complexes shown are neutral complexes, so we can calculate the d^n configuration of each metal by taking their valence electrons less the oxidation state:

1



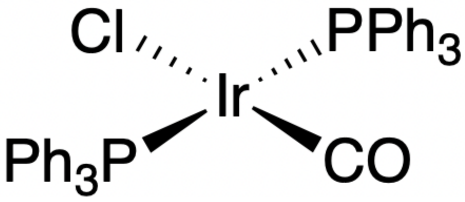
$d^n = 9 - 1 = 8$

2



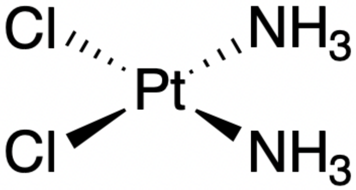
$d^n = 10 - 0 = 10$

3



$d^n = 9 - 1 = 8$

4

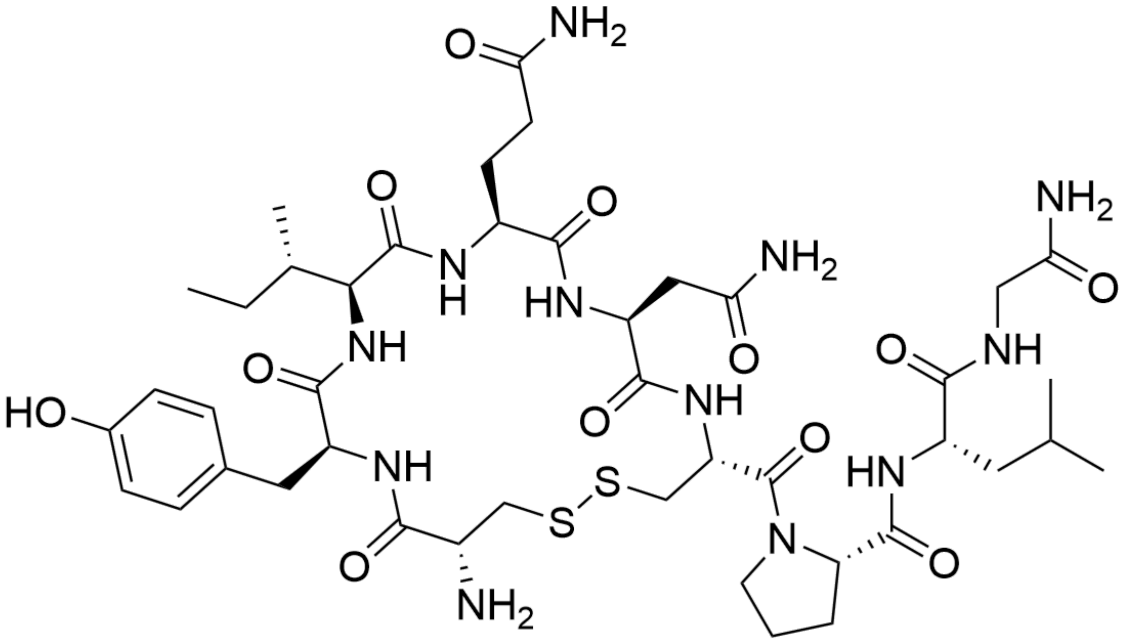


$d^n = 10 - 2 = 8$

Problem prepared by: Lin Bohan

AR22: Makin' It All Okay

Oxytocin is a hormone that plays an important role in love, sexual activity, and reproduction in humans. The full chemical structure of oxytocin is shown below.



If oxytocin was refluxed with excess dilute HCl and neutralised (so that all amino acids exist as zwitterions), what is the M_r of the organic product with the **highest** molecular weight?

Leave your answer to the nearest integer.

Solution:

240

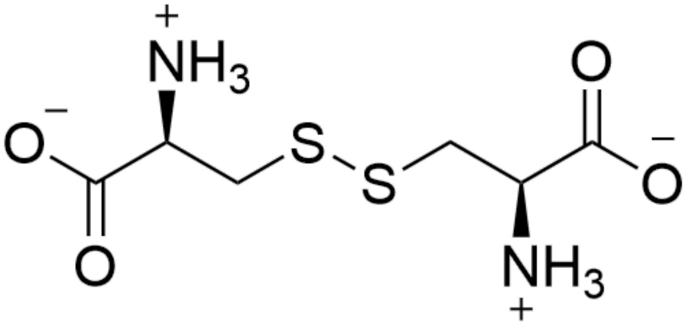
Oxytocin is a peptide consisting of 9 amino acids with the sequence cysteine–tyrosine–isoleucine–glutamine–asparagine–cysteine–proline–leucine–glycine–NH_2 (the −COOH end of glycine is converted to a primary amide). When heated under acidic conditions, the amide bonds will hydrolyse.

The cysteine residues in oxytocin are connected via a disulfide bridge (R—S—S—R). These require a reducing agent such as dithiothreitol or sodium borohydride to reduce the disulfide bond to a thiol, so they are spared from acidic hydrolysis.

$$\text{R—S—S—R} + 2\,[\text{H}] \rightarrow 2\,\text{R—SH}$$

Hence, the resultant organic product with two cysteine molecules (shown below) connected via a disulfide bond, $C_6H_{12}O_4N_2S_2$, has the highest M_r at $6(12.01) + 12(1.008) + 4(16) + 2(14.01) + 2(32.07) =$ **240** (3 s.f.)

The next highest is tyrosine with a M_r of 181.



Problem prepared by: Wang Jiahua

AR23: Introverted Electrons

Which of the following cations have the same number of unpaired electrons?

A	B	C	D	E
$^{52}Co^{3+}$	$^{192}Os^{4+}$	$^{54}Cr^{3+}$	$^{40}S^{2+}$	$^{141}Pr^{3+}$

Leave your answer as a concatenated string of ***capital letters*** *in ascending alphabetical order. For example, if A, B and D have the same number of unpaired electrons, leave your answer as "ABD".*

Solution:

ABE

We need to outline the electronic configuration for each of these cations; the nucleon number bears no significance on the ions' electron configuration. The proton number of each cation is included instead.

	cation	electronic configuration of atom / cation	no. of unpaired electrons
A	$_{27}Co^{3+}$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ [↿⇂][↿][↿][↿][↿] 3d	4
B	$_{76}Os^{4+}$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^6\ 6s^2$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^4$	4
C	$_{24}Cr^{3+}$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$	3
D	$_{16}S^{2+}$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$	2
E	$_{59}Pr^{3+}$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^3\ 5s^2\ 5p^6\ 6s^2$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^3\ 5s^2\ 5p^5$ [↿⇂][↿⇂][↿] 5p	3 + 1= 4

Since $_{27}Co^{3+}$, $_{76}Os^{4+}$ and $_{59}Pr^{3+}$ all have 4 unpaired electrons, the answer is ABE.

It is vital to remember that electrons are removed from the valence shells, so the electronic configuration of each atom needs to be determined first.

The setter recommends enlisting the help of online sources such as ptable.com to ascertain the electronic configurations of the atoms rather than doing so manually.

Problem prepared by: Lie Huan Yew

AR24: Want Some Pudding?

According to the plum-pudding model, an atom consists of electrons surrounded by a spherical volume of positive charge. An experiment involves firing a cuboidal volume of many alpha particles onto a single atom.

Assume that:

1. Deflections of the alpha particle is caused by direct contact with the spherical volume of positive charge
2. The length of the cuboid equals the diameter of the sphere

What fraction of the alpha particles will be **scattered**?

Leave your answer as a decimal to 3 significant figures.

Solution:

0.785

Contact of the cuboidal volume of alpha particles onto the hemisphere of the atom facing it accounts for all deflections. This can be simplified to the following: what is the probability of a random point on a unit square falling on a unit circle? It simply is $\frac{\pi r^2}{(2r)^2} = \frac{\pi}{4} = 0.785$ (3 s.f.)

Problem prepared by: Chua Ming Xiu

AR25: Exploding Vials

In a stroke of inspiration, Jorge decides to explode a glass vial by injecting CO_2 into it (please do not repeat this experiment at home). A rudimentary Google search reveals that the average borosilicate lab apparatus can withstand 25 psi of pressure before exploding.

To explode an evacuated 280 ml glass vial at r.t.p, what mass of CO_2 in grams will Jorge need to obtain? Assume ideal gas behaviour, and use the following data: 1 psi = 6894.76 Pa.

Leave your answer to 3 significant figures.

Solution:

871

$$\begin{aligned}
pV &= nRT = \frac{m}{M_r}RT \\
m &= \frac{pVM_r}{RT} \\
&= \frac{25(6894.76)(280 \times 10^{-6})(12.01 + 2 \times 16.00)}{8.3145(293.15)} \\
&= 0.871 \text{ kg} \\
&= 871 \text{ g}
\end{aligned}$$

Problem prepared by: Lin Bohan

AR26: Stubborn Bismuth

The only primordial isotope of bismuth, ^{209}Bi, was found to undergo α-decay in 2003 with an extremely long half-life of 2.01×10^{19} years to form ^{205}Tl. This is many magnitudes greater than the current age of the universe, and for all intents and purposes, bismuth can be considered stable.

At this moment, I have a 5 cm cube of 100% pure solid bismuth (density = 9.807 g cm^{-3}). Theoretically, how many seconds must we wait until a **single** atom of bismuth in this cube undergoes radioactive decay?

Assume that there are 24 hours in a day, and 365 days in a year.

Leave your answer to 2 significant figures.

Solution:

260

Decay constant of ^{209}Bi, $\lambda = \frac{\ln(2)}{2.01\times10^{19}} = 3.4485 \times 10^{-20}$ years^{-1}

Mass of cube = $5^3 \times 9.807 = 1225.875$ g

Number of ^{209}Bi atoms initially = $\frac{1225.875}{209} \times 6.0221 \times 10^{23} = 3.5322 \times 10^{24}$

Using the formula $N = N_0 e^{-\lambda t}$,

$$t = -\frac{1}{\lambda}\ln\left(\frac{N}{N_0}\right)$$

$$= -\frac{1}{3.4485\times10^{-20}}\ln\left(\frac{3.5322\times10^{24}-1}{3.5322\times10^{24}}\right)$$

$$= 8.2097 \times 10^{-6} \text{ years}$$

$$= 8.2097 \times 10^{-6} \times 365 \times 24 \times 60 \times 60 \text{ seconds}$$

$$\approx \mathbf{260} \text{ s (2 s.f.)}$$

The same answer can also be found by calculating the activity of the bismuth cube, using the formula $A = \lambda N$.

Problem prepared by: Wang Jiahua

AR27: Redox I

Fully balance the following ionic equation:

$$\boldsymbol{a}\,N_2O_4 + \boldsymbol{b}\,Br^- + \boldsymbol{c}\,OH^- \rightarrow \boldsymbol{d}\,NO_2^- + \boldsymbol{e}\,BrO_3^- + \boldsymbol{f}\,H_2O$$

Find the minimum sum of integer coefficients $\boldsymbol{a}$ to $\boldsymbol{f}$.

Solution:

20

$$\boldsymbol{a}\,N_2O_4 + \boldsymbol{b}\,Br^- + \boldsymbol{c}\,OH^- \rightarrow \boldsymbol{d}\,NO_2^- + \boldsymbol{e}\,BrO_3^- + \boldsymbol{f}\,H_2O$$

This is a typical redox reaction. We find that the oxidation state of Br increases from –1 in Br^- to +5 in BrO_3^-, while the oxidation state of N decreases from +4 in N_2O_4 to +3 in NO_2^-. Constructing half equations and balancing them will solve this problem.

$$Br^- \rightarrow BrO_3^-$$
$$Br^- + 6\,OH^- \rightarrow BrO_3^- + 3\,H_2O$$
$$Br^- + 6\,OH^- \rightarrow BrO_3^- + 3\,H_2O + 6\,e^-$$

$$N_2O_4 \rightarrow NO_2^-$$
$$N_2O_4 \rightarrow 2\,NO_2^-$$
$$N_2O_4 + 2\,e^- \rightarrow 2\,NO_2^-$$

Putting these together,

$$3\,N_2O_4 + Br^- + 6\,OH^- \rightarrow 6\,NO_2^- + BrO_3^- + 3\,H_2O$$

The sum of the coefficients is therefore 3 + 1 + 6 + 6 + 1 + 3 = 20.

Problem prepared by: Lie Huan Yew

AR28: BlueBlackPink

All unknown compounds in this question have a common element, **X**.

Compound **A** is black. Upon heating compound **A** with oxygen gas at high temperatures, a pink substance **B** is formed. At lower temperatures, a red solid **C** is formed instead. On the addition of concentrated ammonia solution, a colourless solution is formed, and on standing, this solution turns blue, containing compound **D**. Upon addition of dilute sulfuric acid, then ethanol to compound **D**, a blue solid, compound **E** is formed.

What is the electronic configuration of element **X** in *spdf* notation?

Leave your answer without subscripts or spaces, in increasing principal quantum numbers. If your answer is neon, for example, leave your answer as 1s22s22p6. If your answer is xenon, for example, leave your answer as 1s22s22p63s23p63d104s24p64d105s25p6.

Solution:

1s22s22p63s23p63d104s1

Firstly, we know that the element is most likely a transition metal, given the different colour it exhibits.

Next, we can guess that the element is copper, as there are many clues pointing to this in the question:

> *On the addition of concentrated ammonia solution, a colourless solution is formed, and on standing, this solution turns blue, containing compound **D**.*

This is characteristic of copper(I) oxide. Cu_2O dissolves in concentrated ammonia solution to form the colourless complex $[Cu(NH_3)_2]^+$, which is then oxidised to the blue copper tetraamine complex.

> *Upon heating compound **A** with oxygen gas at high temperatures, a pink substance **B** is formed.*

This is a typical redox reaction. $Cu_2S + O_2 \rightarrow 2\ Cu + SO_2$, and copper is the pink solid mentioned.

> *At lower temperatures, a red solid **C** is formed instead.*

This is typical of Cu_2O. Cu_2S indeed undergoes a redox reaction to form SO_2 and Cu_2O.

Now, the electronic configuration of Cu is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$, not $3d^9\ 4s^2$!

This gives the final answer of **1s22s22p63s23p63d104s1**.

Problem prepared by: Lim Dillion

AR29: Phasing Through The Floor

The pressure-volume behaviour of nitrogen gas can be expressed through the following Van der Waals equation, where P is in bar, V is in dm^3, $R = 8.3145$ J mol^{-1} K^{-1}, T is in K, and the numbers are such that the equation is dimensionally constant:

$$P = \frac{RT}{V - 0.0387} + \frac{1.37}{V^2}$$

When considering the different phases of a substance, the liquid-vapour **critical point** is where phase boundaries vanish, and a liquid and its vapour can coexist.

The condition for the critical point to exist is for there to be a stationary point of inflection on the pressure-volume diagram. That is,

$$\frac{\partial P}{\partial V} = 0, \text{and } \frac{\partial^2 P}{\partial V^2} = 0 \; .$$

Find the volume, in cm^3, for which nitrogen has a critical point.

Leave your answer to 1 decimal place.

Solution:

116.1

We simply differentiate with respect to *V*, and find the point where both are zeroes. This can be done manually fairly quickly, or can even be done with an online calculator (Wolfram Alpha, DerivativeCalculator, etc.).

$$\frac{\partial P}{\partial V} = 0 \Rightarrow RTV^3 = -2.74(V - 0.0387)^2$$

$$\frac{\partial^2 P}{\partial V^2} = 0 \Rightarrow 2RTV^4 = -8.22(V - 0.0387)^3$$

Dividing the equations, $2V = 8.22/2.74(V - 0.0387)$

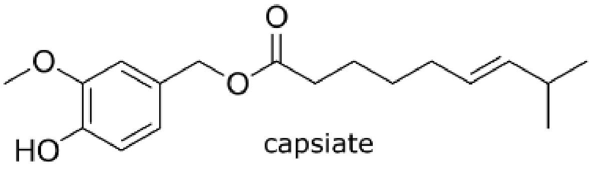
$$V = 3 \cdot 0.0387 = 0.1161 \text{ dm}^3 = \mathbf{116.1\ cm^3}$$

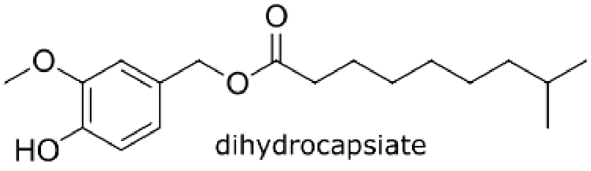
Problem prepared by: Lim Dillion

AR30: Spicy Separation

When we eat peppers, our tongues often burn, and we call this taste “spiciness”. Capsinoids are a class of chemical compounds that give rise to this taste.

The most straightforward examples of capsinoids are capsiate and dihydrocapsiate, two very similar compounds:


capsiate


dihydrocapsiate

I have a sample of capsiate and dihydrocapsiate, but I forgot which bottle is which! And… I forgot to label my bottles.

Which of the following chemical tests can distinguish between both samples?

- A) Add bromine water to a sample of each compound.
- B) Add bromine in CCl_4 to a sample of each compound.
- C) Add concentrated HNO_3, followed by bromine water to a sample of each compound.
- D) Add cold, alkaline $KMnO_4$ to a sample of each compound.
- E) Add hot $KMnO_4$ with aqueous H_2SO_4 to a sample of each compound.

Leave your answer as a concatenated string of ***capital letters*** *in ascending alphabetical order. For example, if you believe A, B and D are correct, leave your answer as “ABD”.*

Solution:

CD

At first glance, one might think that all of these could distinguish the compounds! But this is not necessarily true.

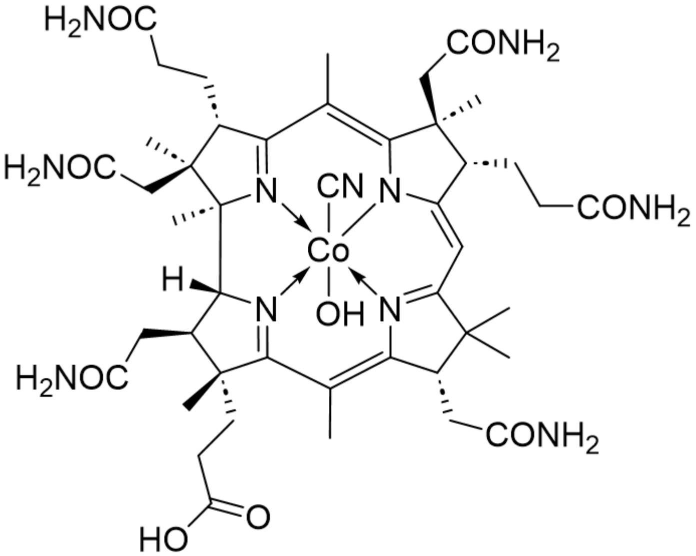
- Bromine water will also react with the phenol group in both compounds, decolourising it. So **A** will not work.
- Br_2 in CCl_4 can still undergo monosubstitution with the phenol group, so **B** does not work.
- Concentrated HNO_3 will nitrate any positions on the aromatic group that might undergo substitution with the Br_2, so after adding concentrated HNO_3, Br_2 will only react with the alkene groups. So **C** works.
- Cold, alkaline $KMnO_4$ will decolourise and brown precipitate will form upon addition to the alkene-containing compound. Option **D** works.
- Hot, acidic $KMnO_4$ will decolourise for both compounds because of side-chain oxidation with the alkyl side-chain of the aromatic group, so **E** will not work.

Therefore, we are left with options **C** and **D** which work.

Problem prepared by: Lim Dillion

AR31: Cobyric Acid

Vitamin B12, also known as cobalamin, is a water-soluble vitamin involved in metabolism. In the 1960s, it was shown that cobyric acid can be easily transformed into vitamin B12. The structure of cobyric acid is shown below. It is known that the shape about its cobalt centre is octahedral.

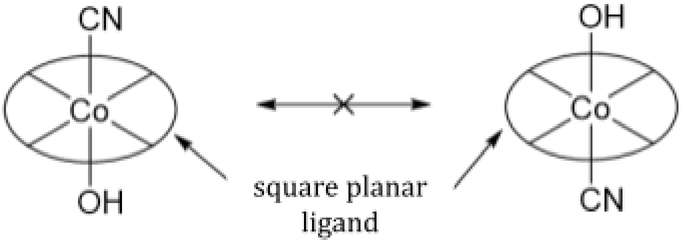


How many stereoisomers does cobyric acid have, including the stereoisomer shown above?

Solution:

1024

There are 9 chiral carbons in cobyric acid. Although there is restricted rotation about the C=C double bonds in cobalamin, these C=C groups cannot exhibit cis-trans isomerism as their counterpart will be too strained to be stable. However, the Co centre can exhibit stereoisomerism, as shown in the diagram below.



Hence, there are $2^9 \times 2 =$ **1024** stereoisomers of cobyric acid.

Problem prepared by: Ranen Yong

AR32: Elementary Reactions

An elementary reaction proceeds via the scheme $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C}$.

1 mol of soluble solid **B** is added to a 1 dm^3 solution of **A** to start the reaction, and aliquots of the reaction mixture are taken at intervals to monitor the changes in value of [**A**].

The value of [**A**] before the addition of **B** is 0.00500 mol dm^{-3}. After 10.0 s, the value of [**A**] has decreased to 0.00300 mol dm^{-3}.

Find the rate constant k of the reaction, in units of $mol^{-1}\ dm^3\ s^{-1}$.

Leave your answer to 2 significant figures.

Solution:

0.051

To find out how [**A**] varies with changes in t, we can apply the integrated rate law.

From the reaction equation, we can write $rate = -\frac{d[A]}{dt} = k[A][B]$. However, since the large initial excess of **B** (1 mol of **B** compared with 0.005 mol of **A**) would leave the value of [**B**] roughly unchanged over the reaction, we note that we can disregard [**B**] in the rate equation. The reaction is hence pseudo-first order with respect to **A**, and we can re-express $k[B]$ as a new constant k'.

$$-\frac{d[A]}{dt} = k'[A] \Rightarrow \frac{1}{[A]}d[A] = -k'dt$$

Given [**A**] = 0.00500 when t = 0 and [**A**] = 0.00300 when t = 10.0, we can integrate both sides with respect to t, over this interval.

$$\int_{0.00500}^{0.00300} \frac{1}{[A]}d[A] = -\int_{0}^{10.0} k'\,dt$$

$$[ln[A]]_{0.005}^{0.003} = -[k't]_{0}^{10.0}$$

$$-k'(10.0 - 0) = ln(0.003) - ln(0.005)$$

$$10.0k' = ln(0.005) - ln(0.003)$$

$$\Rightarrow k' = 0.051083\ \text{s}^{-1}\ \text{(5 s.f.)}$$

Recall that $k' = k[B]$, where [**B**] remains roughly constant at 1.00 mol dm^{-3}.

Therefore $k = \frac{0.051083}{1.00}$ = 0.051 mol^{-1} dm^{3} s^{-1} (2 s.f.)

Problem prepared by: George Zhou

AR33: Try ⇌ Die

You may be familiar with the dimerisation of monomers such as CH_3CO_2H and NO_2, but what happens when the monomer has a particular disdain for isolation? A vast majority of aluminium alkoxides tend to form cyclic oligomers owing to the coordinative unsaturation about the central Al atom. Consider the following equilibrium:

$$2\,[Me_2AlOEt]_3 \rightleftharpoons 3\,[Me_2AlOEt]_2 \qquad \begin{array}{l}\Delta H^\ominus = 85.0\text{ kJ}\\ \Delta S^\ominus = 218\text{ J K}^{-1}\end{array}$$

Calculate the mole fraction of the monomer Me_2AlOEt existing as the trimer $[Me_2AlOEt]_3$ at 100°C. The initial monomer concentration is 2.5 mol dm^{-3}.

Leave your answer to 3 significant figures.

Hint: The following equations will be helpful:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$
$$\Delta G^\ominus = -RT\ln K_{eq}$$

Solution:

0.643

Let the mole fraction of the monomer existing as the trimer be x. The mole fraction of the monomer existing as the dimer is therefore $(1 - x)$. We can then express the equilibrium constant in terms of x:

$$K_{\mathrm{eq}} = \frac{[dimer]^3}{[trimer]^2} = \frac{\left[2.5\times\frac{1-x}{2}\right]^3}{\left[2.5\times\frac{x}{3}\right]^2} = 2.8125 \times \frac{(1-x)^3}{x^2}$$

It is vital to divide the concentrations by 2 for the dimer and 3 for the trimer since the mole fractions describe the monomers.

We can form an expression involving only x using some manipulation:

$$\Delta G^\ominus = \Delta H^\ominus - \mathrm{T}\Delta S^\ominus = -RT\ln K_{\mathrm{eq}}$$
$$\ln K_{\mathrm{eq}} = \frac{1}{R}\left(\Delta S^\ominus - \frac{\Delta H^\ominus}{T}\right)$$

Substituting the values $\Delta H^\ominus = 85.0$ kJ, $\Delta S^\ominus = 218$ J K^{-1}, $T = 373.15$ K,

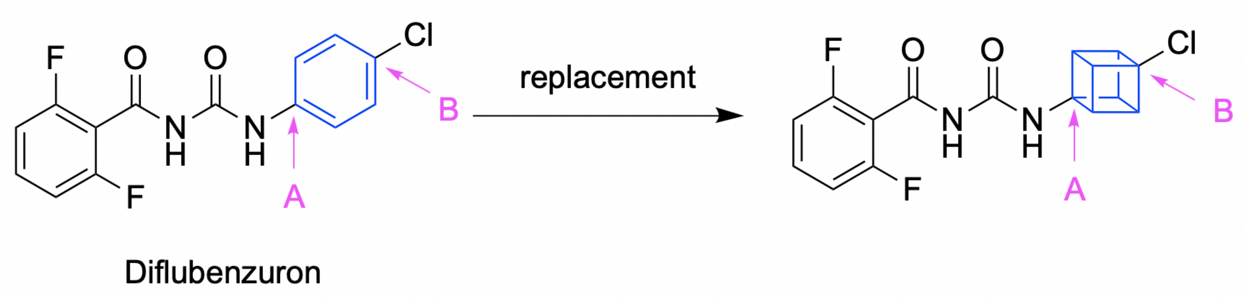
$$2.8125 \times \frac{(1-x)^3}{x^2} = e^{\frac{1}{8.3145}\left(218-\frac{85000}{373.15}\right)}$$

Solving this equation gives us $x = 0.643$ (3 s.f.).

Problem prepared by: Lie Huan Yew

AR34: Drugs[3]

Cubane is being investigated in pharmaceutical applications owing to its ability to link key moieties at a specific distance extremely similar to benzene. For example, the phenyl ring in diflubenzuron has been replaced by cubane in the hopes of altering its biochemical properties:



Given that the bond length of a C—C single bond is 154 pm and that of an aromatic C=C bond is 139 pm, what is the value of $\frac{\text{distance between A and B in the cubane analogue}}{\text{distance between A and B in diflubenzuron}}$?

Leave your answer to 5 significant figures.

Solution:

0.95948

In diflubenzuron, the distance is simply twice an aromatic C=C bond, i.e 278 pm.

In the cubane analogue, the distance is the distance from one vertex of a cube of length 154 pm to the opposite vertex, which can be obtained as $154\sqrt{3}$ pm. (The diagonal distance of a face of a cube of length u is $u\sqrt{2}$, and then by Pythagoras' theorem, from one vertex to another it is ($\sqrt{(u\sqrt{2})^2 + u^2} = u\sqrt{3}$.)

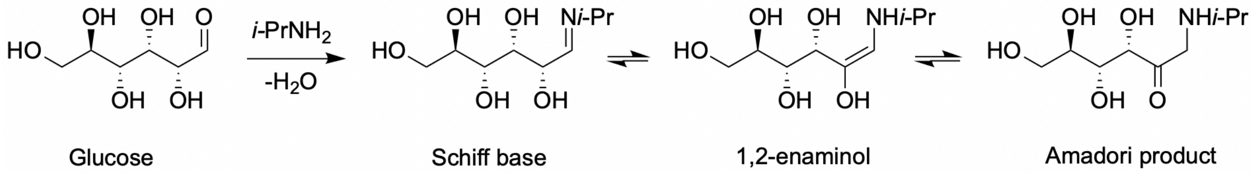
The ratio is $\frac{154\sqrt{3}}{278} = 0.95948 \text{ (5 s.f.)}$. As you can see the distances are really quite close!

Problem prepared by: Lin Bohan

AR35: Who Let Him Cook?

When we cook, many reactions happen to give rise to the characteristic taste of certain foods. One such reaction is the **Maillard reaction**.

The first step of the Maillard reaction involves a reaction between the aldehyde group of a sugar and the amino group of an amino acid to form a glycosylamine. The next step of the Maillard reaction involves an Amadori rearrangement. The glycosylamine undergoes a rearrangement to form a ketosamine. The Amadori compound can then further react to form other compounds that give rise to the typical taste of foods.



Tim has a raw steak. He wants to make it undergo the Maillard reaction so that he can enjoy a nice dinner.

Barring the taste of the final steak, which of the following common cooking additives in the table below, when added to the steak, can possibly **speed up** the Maillard reaction and allow Tim to have a "nice" dinner?

A) Lye (NaOH)	**E)** Calcium chloride
B) Vinegar	**F)** MSG (Monosodium Glutamate)
C) Water	**G)** Vanillin
D) Catechin	**H)** Sorbic acid

*Leave your answer as a string of **capital letters** in ascending alphabetical order. For example, if A, B and D can speed up the Maillard reaction, leave your answer as "ABD".*

Solution:

AEFH

Overall, the main cause of a slow Maillard reaction is an acidic cooking environment (not always, though, as we will see below). This is because acids will protonate the amine in the amino acid and thereby reduce its nucleophilicity, making the first step of the Maillard reaction, a nucleophilic substitution (as seen in the mechanism), much slower.

A) **Lye** is often used to speed up the Maillard reaction by deprotonation of the amino acid. In fact, Lye rolls are a baked specialty in many European countries, made by dunking bread in lye.

B) **Vinegar** being acidic and often having high water content, this both reduces the nucleophilicity of the amino acid, and also reduces the concentrations of the reactants.

C) **Water** slows down the reaction (see **B**).

D) **Catechin** can react with the amino acid through a Michael addition to form an amine-quinone adduct, significantly slowing down the reaction.

E) **Calcium Chloride** is a good desiccant, drawing water out from food and thereby increasing the rate of reaction by increasing concentration of reactants.

F) **Monosodium Glutamate** - This is one special case where we can speed up the rate of reaction not by deprotonation of the amine, but by increasing the concentration of reactants (i.e. the amino acid).

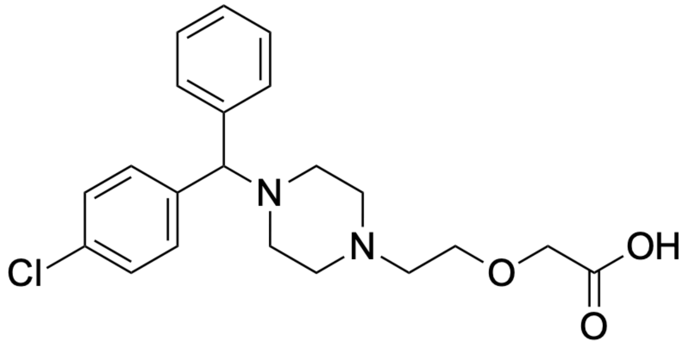
G) **Vanillin** has almost no effect on the Maillard reaction.

H) **Sorbic acid** - Interestingly, although this is an acid, it actually speeds up the rate of the Maillard reaction. Sorbic acid, when in food, rapidly undergoes autoxidation to form carbonyl compounds, which can react with amino acids in the Maillard reaction, speeding it up.

Problem prepared by: Lim Dillion

AR36: Allergies

Cetirizine, a common antihistamine found in brands like Zyrtec, is used to relieve allergy symptoms.



cetirizine

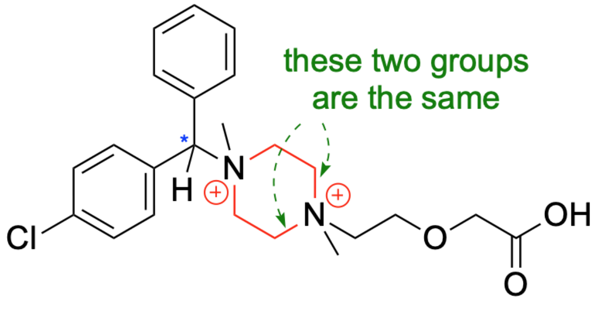
Cetirizine can react with excess iodomethane. How many chiral centres does the product of this reaction have?

Solution:

1

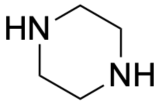
The original cetirizine contains 1 chiral centre at the benzylic position (marked in blue).

When the tertiary amine groups undergo a nucleophilic substitution reaction with iodomethane, quaternary ammonium cations are formed, which may be able to display chirality.



cetirizine

However, since there are two groups that are the same due to the symmetrical piperazine ring, the quaternary ammonium cations are not chiral.



piperazine

Hence, the answer is 1, due to the original chiral centre present in cetirizine (marked in blue).

Problem prepared by: Timothy Chek

AR37: Electrifying!

In acidic solution, technetium undergoes the following half reactions:

Redox **unbalanced** half-equation	Cell potential / V
$TcO_4^- \rightarrow TcO_3$	+0.700
$TcO_4^- \rightarrow TcO_2$	+0.738
$TcO_4^- \rightarrow TcO_4^{2-}$	–0.569
$TcO_3 \rightarrow Tc$	+0.434
$TcO_4^{2-} \rightarrow TcO_2$	**(1)**
$TcO_2 \rightarrow Tc$	**(2)**

What are the cell potentials **(1)** and **(2)**? Concatenate your answers to both, in order, and include the sign (+ or –). For example, if the cell potential **(1)** is +0.420V and the cell potential **(2)** is –0.690V, leave your answer as +0.420–0.690.

Leave your answer as a string. Each of the cell potentials should be given to 3 significant figures.

Solution:

+1.39+0.273

Firstly, let's consider the cell potential of TcO_4^- → Tc. Recall that electrode potentials are **not additive**.

$$\text{Electrode potential} = \frac{+0.700 \times 1 + 0.434 \times 6}{7} = +0.472\ \text{V}.$$

Next, we can directly compute **(1)**, using the data above from the +7 oxidation state to the +6 and +4 oxidation state .

$$\text{Electrode potential} = \frac{+0.738 \times 3 - (-0.569) \times 1}{2} = +1.39\ \text{V (3 s.f.)}.$$

Lastly, we have all the information we need to compute **(2)**.

$$\text{Electrode potential} = \frac{+0.472 \times 7 - (+0.738) \times 3}{4} = +0.273\ \text{V (3 s.f.)}.$$

Problem prepared by: Lim Dillion

AR38: Diabolical Oxide

Jorge refluxes 9.440 grams of a metal oxide $\mathbf{M}_x\mathrm{O}_7$ with excess dilute hydrochloric acid. When he filters the mixture, 4.821 grams of an insoluble anhydrous oxide is obtained. Upon crystallisation, he obtains another 9.428 grams of a metal chloride hexahydrate. No other products containing **M** were formed.

It is given that $\mathbf{M}_x\mathrm{O}_7$ contains **M** in 2 different oxidation states, which were then separated. The chloride contains the lower oxidation state.

If the atomic number of **M** is y, what is the value of xy?

Solution:

260

The higher oxidation state of M must have ended up in the oxide, while the lower is in the chloride.

We can perform guess-and-check using different values of x, starting with $x = 2$. However, that would mean an oxidation state of +8 and above for M. M_2O_7 would be a very strong oxidiser (think MnO_4^-), strong enough to liberate chlorine or oxygen from hydrochloric acid. Since no other products were formed and there was no redox reaction, $x = 2$ is unlikely.

What if $x = 3$? One unit of M_3O_7 containing one M^{6+} and two M^{4+} atoms is possible. Suppose M^{6+} and M^{4+} are separated into the oxide and chloride respectively. Let z be the relative atomic weight of M.

$$M_3O_7 \rightarrow MO_3 + 2\ MCl_4 \cdot 6H_2O$$

$$\text{moles of } M_3O_7 = \text{moles of } MO_3$$

$$\frac{9.440}{3z+7(16)} = \frac{4.821}{z+3(16)}$$

$$z = -17.2$$

Oops! Turns out, if we try other combinations of oxidation states (one M^{4+} and two M^{5+}; one M^{2+} and two M^{6+}), we also won't get sensible values for z.

What if $x = 4$? One possible combination is two M^{4+} and two M^{3+} atoms. If we try that,

$$M_4O_7 \rightarrow 2\ MO_2 + 2\ MCl_3 \cdot 6H_2O$$

$$2 \times \text{moles of } M_4O_7 = \text{moles of } MO_2$$

$$\frac{2\times 9.440}{4z+7(16)} = \frac{4.821}{z+2(16)}$$

$$z = 158.9$$

$$2 \times \text{moles of } M_4O_7 = \text{moles of } MCl_3 \cdot 6H_2O$$

$$\frac{2\times 9.440}{4z+7(16)} = \frac{9.428}{z+3(35.45)+6(18.016)}$$

$$z = 158.9$$

It works! We find M to be **Terbium (Tb)**. The initial oxide is Terbium(III, IV) Oxide, Tb_4O_7, which indeed exists.

Hence, our final answer is $65 \times 4 =$ **260.**

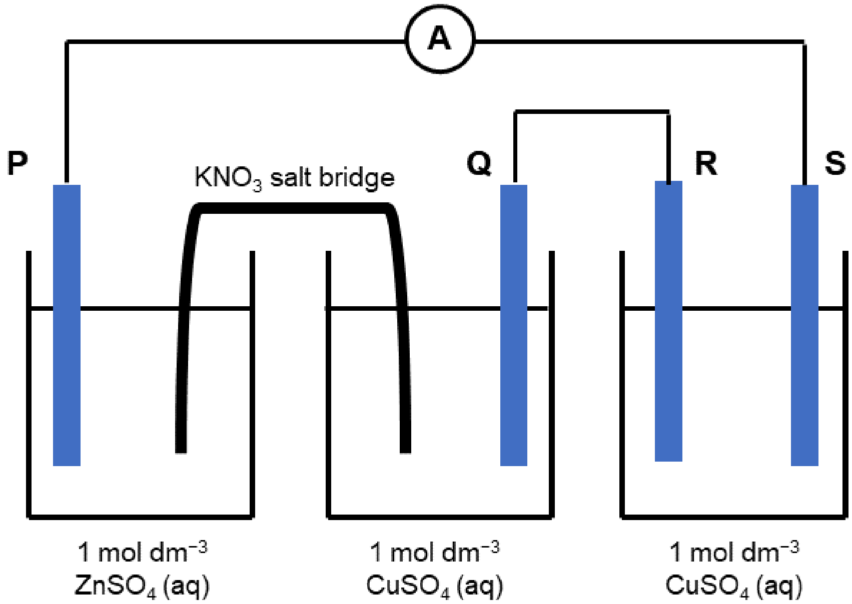
And in case you're wondering, the full reaction that occurred is:

$$Tb_4O_7\ (s) + 6\ HCl\ (aq) \rightarrow 2\ TbO_2\ (s) + 2\ TbCl_3\ (aq) + 3\ H_2O\ (l)$$

Problem prepared by: Wang Jiahua

AR39: Electrickery

Jorge has just learnt about electrochemistry in school. At home, he assembles the following set-up:



Electrode **P** is made of zinc, while all other electrodes are made of copper. When 0.89 A of current passes through the ammeter for 2 hours, effervescence is observed around only one electrode, where 0.591 dm^3 of a single gas is collected at room temperature and pressure. Suppose one or more reactions may take place simultaneously at any electrode.

Which of the following statements is correct?

A) Current flows from electrode **S** through the ammeter to electrode **P**.
B) Reduction occurs at electrode **P**.
C) Electrode **Q** will slowly increase in size.
D) The only reaction occurring at electrode **R** must be $2\ H_2O\ (l) \rightarrow O_2\ (g) + 4\ H^+\ (aq) + 4\ e^-$.
E) Electrode **S** will weigh approximately 0.55 g more at the end of the experiment.

Leave your answer as a string of ***capital letters*** *in ascending alphabetical order. For example, if A, B and D are correct, leave your answer as "ABD".*

Solution:

ACE

Observe that the first 2 beakers contain a Zn^{2+} | Zn and Cu^{2+} | Cu half-cell respectively, while the last beaker is an electrolysis set-up. In essence, this is an electrochemical cell driving an electrolysis reaction.

A) Current flows from electrode **S** through the ammeter to electrode **P**.

True. This is a standard Zn-Cu galvanic cell, where copper is reduced and zinc is oxidised. **P** and **Q** are the anode and cathode respectively. Electrons flow out of **P** and into **S**, so conventional current must flow the other way.

The standard cell potential is simply $0.34 - (-\ 0.76) = +1.10$ V (since all reactants have standard concentrations).

B) Reduction occurs at electrode **P**.

False. P is an anode, where oxidation of Zn occurs.

C) Electrode **Q** will slowly increase in size.

True. Reduction of Cu^{2+} (aq) to Cu (s) occurs at **Q**.

D) The reaction occurring at electrode **R** is 2 H_2O (l) → O_2 (g) + 4 H^+ (aq) + 4 e^-.

False. We are told that a **single** gas is evolved. The amount of electrons passing through the circuit is $n_e = \frac{It}{F} = \frac{(0.89)(2\times3600)}{96485} = 0.066414$ mol, so $\frac{1}{4}(0.066414) = 0.0166$ mol of O_2 gas would be evolved. This is impossible because $\frac{(101325)(0.591\times10^{-3})}{(8.3145)(293.15)} = 0.024568$ mol of gas was present at the end. Hence the reaction occurring at **R** is simply the oxidation of copper, Cu (s) → Cu^{2+} (aq) + 2 e^-.

E) Electrode **S** will weigh approximately 0.55 g more at the end of the experiment.

True. Consider the reduction half-reactions that can take place at electrode **S**.

Cu^{2+} (aq) + 2 e^- $\rightleftharpoons$ Cu (s)	$E^{\ominus} = +0.34$ V
2 H^+ (aq) + 2 e^- $\rightleftharpoons$ H_2 (g)	$E^{\ominus} = 0.00$ V
SO_4^{2-} (aq) + 4 H^+ (aq) + 2 e^- $\rightleftharpoons$ SO_2 (g) + 2 H_2O (l)	$E^{\ominus} = +0.17$ V

Either H_2 or SO_2 could have been evolved since 2 mol of electrons will evolve 1 mol of either gas.

Suppose 0.024568 mol of SO_2 gas was evolved. The amount of electrons used to reduce SO_4^{2-} is $2(0.024568) = 0.049136$ mol, so $0.066414 - 0.049136 = 0.017278$ mol of electrons were used to reduce Cu^{2+}. $\frac{1}{2}(0.017278) = 0.008639$ mol of Cu (s) was deposited on electrode **S**, increasing its mass by $0.008639 \times 63.55 \approx 0.55$ g.

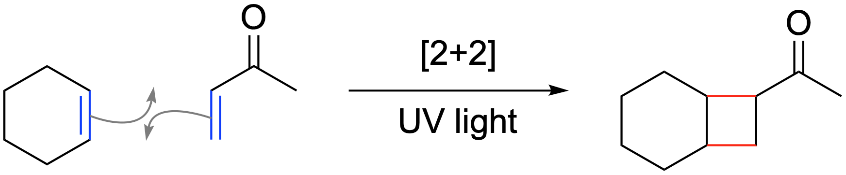
Problem prepared by: Wang Jiahua

AR40: What's As Easy As 2+2=4?

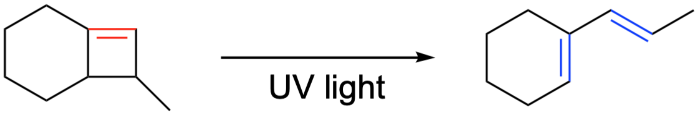
A cycloaddition is a chemical reaction where 2 (or more) pi systems combine through a cyclization, forming a molecule that has fewer pi bonds than the total before.

An example is the [2+2]-cycloaddition between an enone (ket<u>one</u> with a conjugated alk<u>ene</u>) and another alkene under UV light. In this reaction, each of the molecules has 2 pi electrons involved in the reaction. While the enone has a total of 4 pi electrons, the 2 pi electrons that form the C=O bond are not involved.

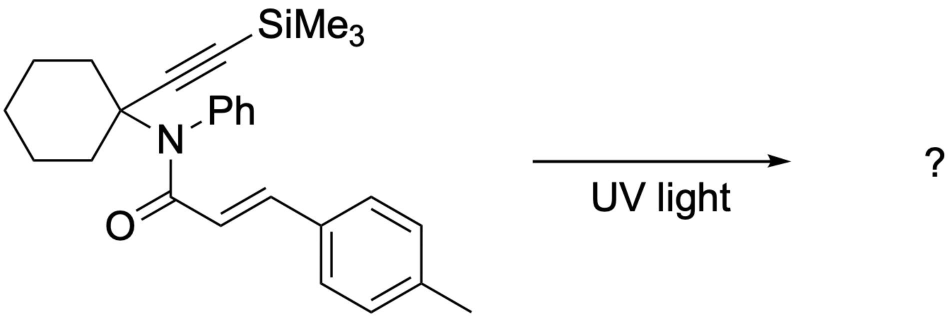
In summary, there is a loss of 2 pi bonds, in exchange for the formation of 2 sigma bonds.

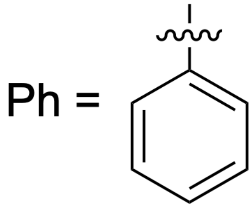


Additionally, it is known that highly strained cyclobutene rings also react under UV light to form dienes, with the product minimising steric hindrance.



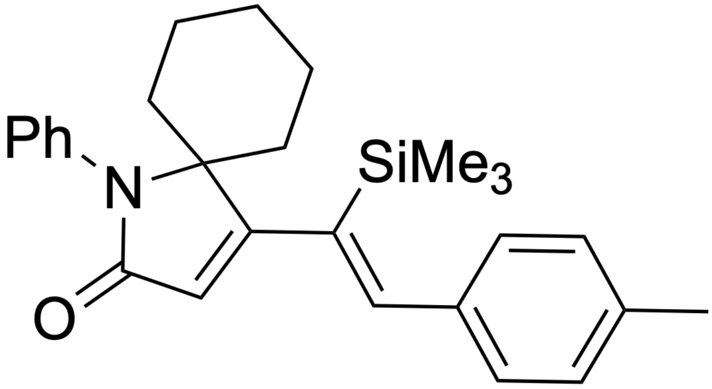
What is the major product of the following reaction?



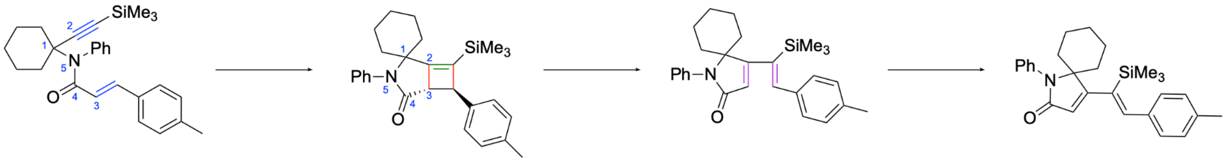


Leave your answer as an organic structure. Omit stereochemistry, if any

Solution:



The starting compound first undergoes a [2+2]-cycloaddition between an enone and an alkyne to yield a cyclobutene ring, which subsequently reacts to give a diene. The alkene with the p-tolyl and –$SiMe_3$ group is (Z) in order to minimise steric hindrance.

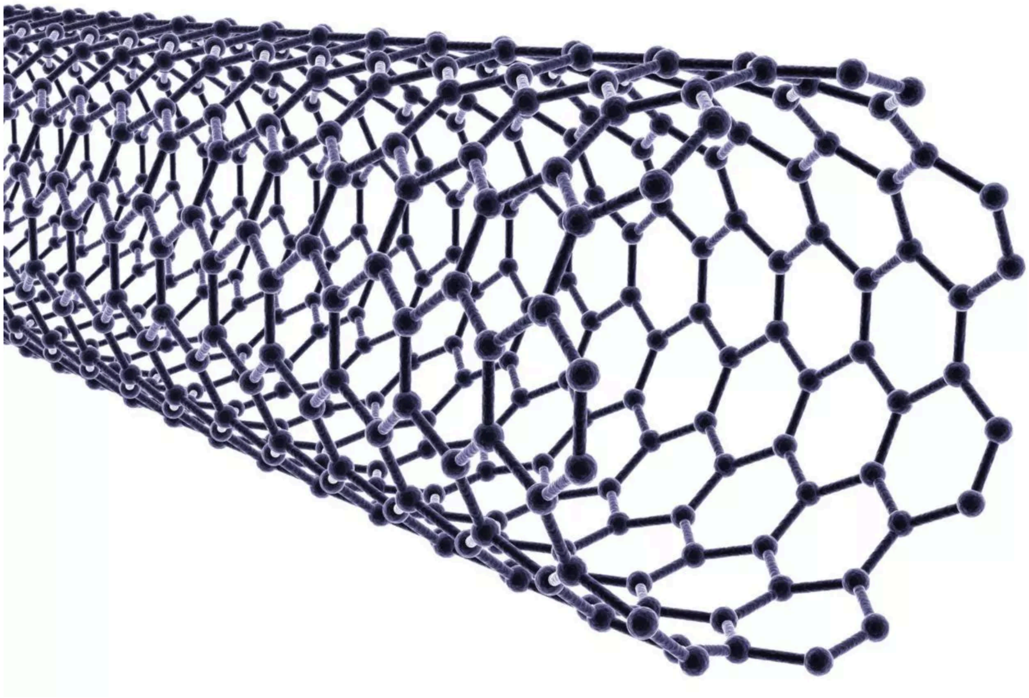


Do note that it is unlikely that the benzene rings are involved in the first cycloaddition, as it will result in a loss of aromaticity that cannot be regained.

Problem prepared by: Timothy Chek

AR41: Perfect Carbon Nanotube

In a hypothetical experiment, 3.191×10^{-14} mol of pure carbon is reacted to form a single, perfectly straight carbon nanotube. This nanotube has an "armchair" structure with a uniform circumference and two open ends, as shown below.



Both ends of the carbon nanotube. The actual number of carbons in the circumference may or may not be the same as shown above[3]*.*

The diameter of the nanotube is 9.2771 nm. Assume all C–C bond lengths are exactly 0.145 nm, all bond angles are 120°, and the carbon atoms themselves do not take up space.

What is the length of the nanotube in millimetres?

Leave your answer to 2 significant figures.

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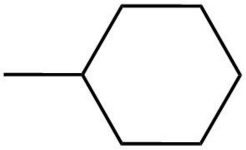
[3] Image source: Harvey, S. (2017, February 21). Promising research for carbon nanotube technology in electrical cabling fabrication - industry articles. All About Circuits. https://www.allaboutcircuits.com/industry-articles/carbon-nanotube-technology-promises-a-revolution-in-cabling/

Solution:

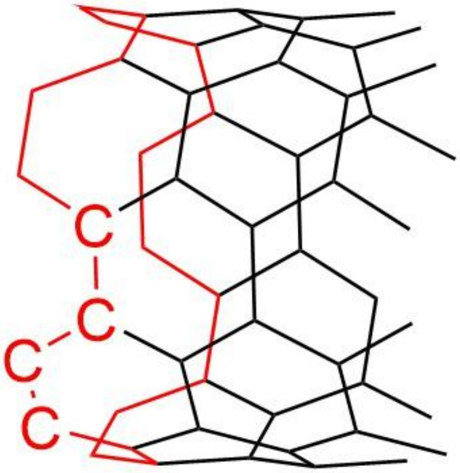
18

Observe that the ends of the nanotube consist of repeated units of the following:



The length of each of these units is $2(0.145) + 2(0.145)(\cos(60°)) = 0.435$ nm. The number of such units in the circumference of the nanotube is $\frac{9.2771\pi}{0.435} = 66.9997 \approx 67$.

We can visualise the nanotube as made up of repeating "layers." One such layer is highlighted in red below. Each layer consists of 67 repeating units of 4 carbons.



Each layer has $67 \times 4 = 268$ carbons, and the perpendicular distance between layers is $2 \times 0.145 \times \sin(60°) = 0.25115$ nm.

Hence the approximate total length of the nanotube is $\frac{(3.191\times10^{-14})(6.0221\times10^{23})}{268} \times 0.25115 = 1.8008 \times 10^{7}$ nm ≈ **18** mm (2 s.f.)

Problem prepared by: Wang Jiahua

AR42: Reaction With Uranium

Excess water is added to 3.802 g of UF_x, where x is an integer. 3.327 g of a solid and a colourless acid are the only products formed under standard conditions of 1 bar and 298.15 K.

What is the value of x?

Solution:

6

Since the reaction is between UF_x and H_2O, it can be deduced that the products contain U, F, H and O. Given the atoms present, the acidic product is most likely HF.

The unbalanced reaction becomes

$$UF_x + nH_2O \rightarrow UO_nF_{x-2n} + 2nHF$$

where n is a whole number.

The quickest way to solve this is to substitute different values of n, and use the mass data given for UF_x and UO_nF_{x-2n} to see if they have a 1:1 molar ratio.

$$\text{Amount of } UF_x = \frac{3.802}{238.0 + x(19.00)} = \frac{3.802}{238 + 19x}$$

$$\text{When } n = 1,$$

$$\text{Amount of } UOF_{x-2} = \frac{3.327}{238.0 + 16.00 + (x-2)(19.00)} = \frac{3.327}{216 + 19x}$$

Equating and solving for x,

$$\frac{3.802}{238 + 19x} = \frac{3.327}{216 + 19x} \implies x = -3.26 \text{ (3 s.f.) which is not possible.}$$

$$\text{When } n = 2,$$

$$\text{Amount of } UO_2F_{x-4} = \frac{3.327}{238.0 + 2(16.00) + (x-4)(19.00)} = \frac{3.327}{194 + 19x}$$

Equating and solving for x,

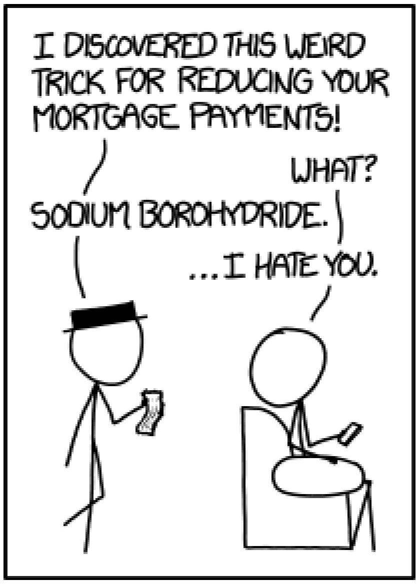
$$\frac{3.802}{238 + 19x} = \frac{3.327}{194 + 19x} \implies x = 6.01 \text{(3 s.f.)} = 6 \text{ (nearest whole no.)}$$

Hence $x = 6$. The balanced reaction is

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

Problem prepared by: Stella Xiao

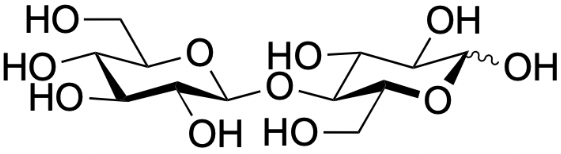
AR43: Reduce Your Payments



Source: https://xkcd.com/1426/

Paper cannot easily be reduced – so $NaBH_4$ may not get rid of your debts.

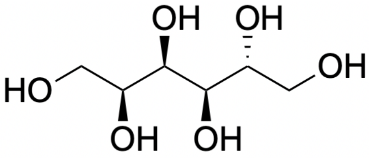
However, cellulose is a major component of paper, and upon treatment with exoglucanase, it forms smaller molecules like cellotriose and cellobiose. The structure of cellobiose is shown below:



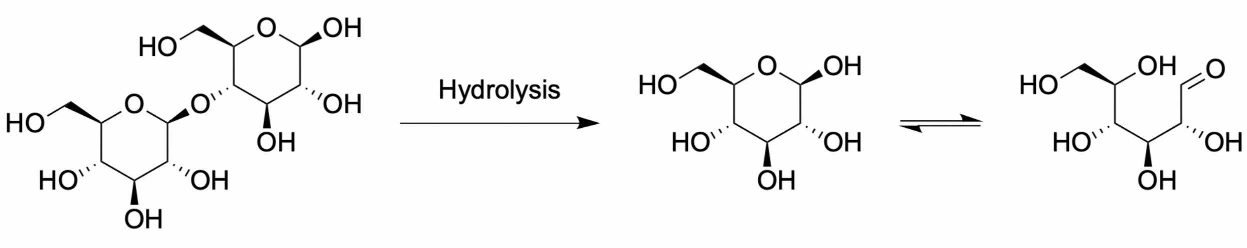
Upon treatment with an acid, then excess $NaBH_4$, what will the end product be? **Include stereochemistry**.

Leave your answer as an organic structure.

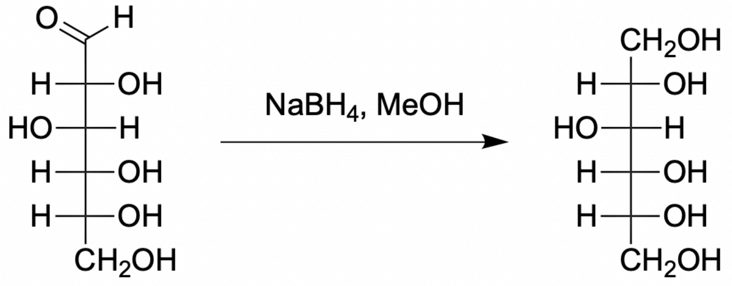
Solution:



In the hydrolysis, the 1,4-glycosidic linkages are hydrolysed to yield 2 glucose molecules:



Rewriting glucose into its fischer projection, we can write the reduction of D-glucose into D-sorbitol, which is our final product:



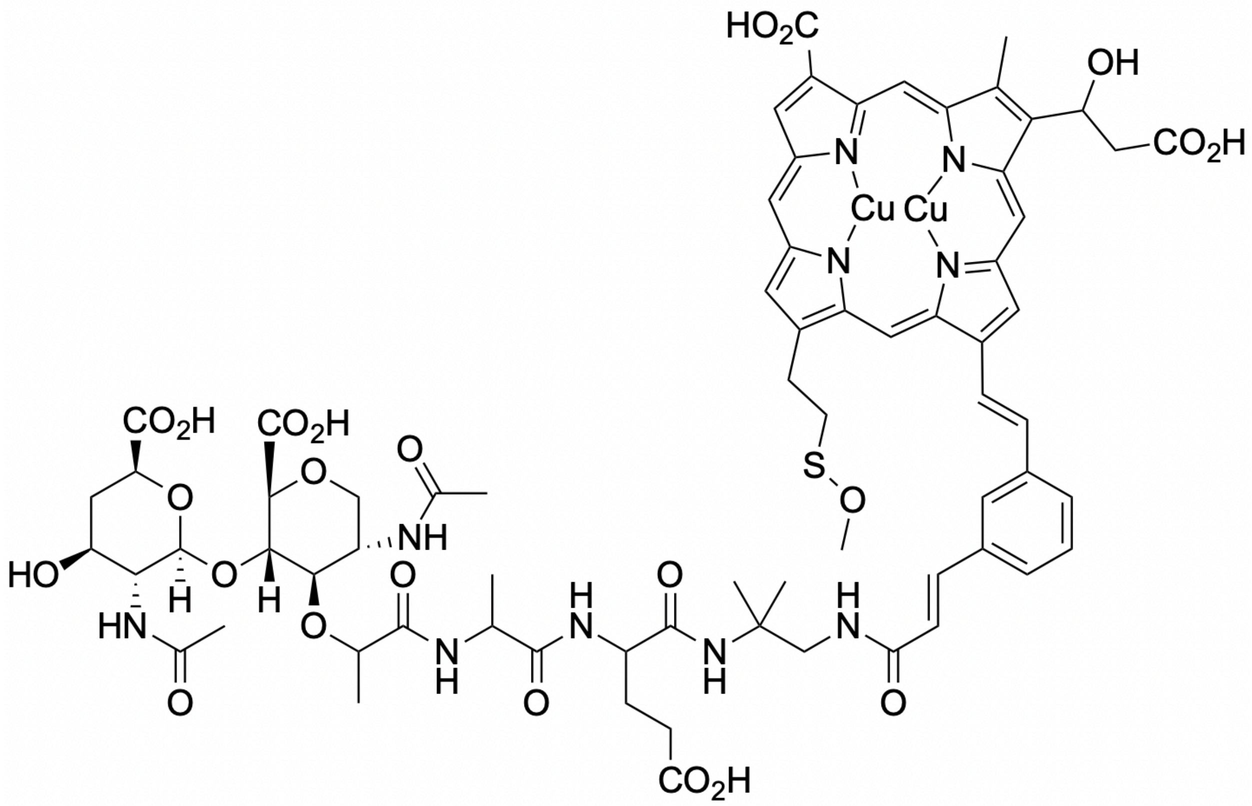
Problem prepared by: Lim Dillion

AR44: The Spice Must Flow

"He who can destroy a thing, controls a thing."

— Paul Atreides

The spice melange in Dune is a herb that gives those who consume it prescient abilities. Its chemical formula is purportedly the one shown below:



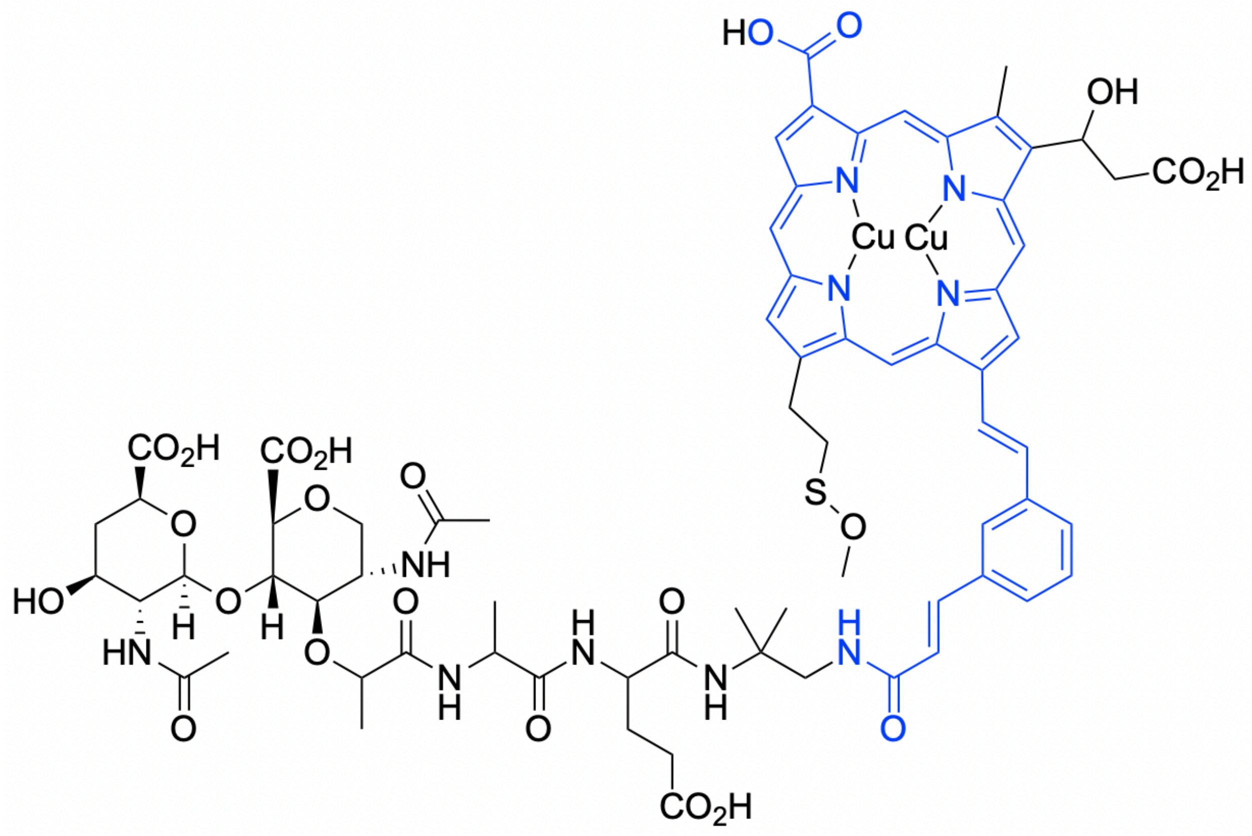
Aside from the horrendous CuCu moiety in the upper right corner, the structure is in fact chemically sound. The likely source of the blue colour is a long, conjugated π system of sp^2-hybridised carbons beginning from the porphyrin ring (that's the huge ring at the upper right) and terminating in the first amide bond from the right.

What is the number of π electrons in this conjugated system?

Solution:

44

The π system is highlighted in blue below:



Each double bond contributes 2π electrons, as does each, N and O when there are no double bonds to it. The total count is 3 such N, 1 such O, and 18 double bonds.

Problem prepared by: Lin Bohan

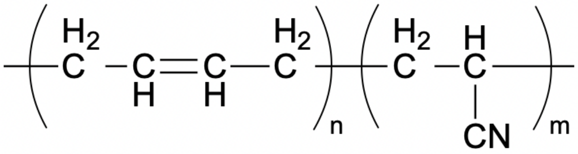
AR45: Lab Safety

A common personal protective equipment (PPE) in labs is a pair of gloves. However, not all gloves are made equal, and using the wrong type of glove can harm you more!

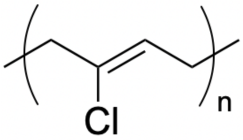
You have the following compounds:

1) 70% nitric acid
2) Dimethyl formamide
3) Furfural
4) Linoleic acid
5) Perchloroethylene
6) Phenol
7) Propylene oxide

There are two common types of gloves in the lab: nitrile gloves and neoprene gloves. Their structures are shown below:



Nitrile gloves



Neoprene gloves

For each of the gloves, indicate whether they will be effective against each of the 7 chemicals. If they are effective, type E, and N if they are not effective. Start with the 7 chemicals against nitrile, then neoprene.

A glove being effective against a chemical means that the glove does not weaken upon prolonged contact with the chemical.

For example, if your answer for nitrile is effective for everything, and your answer for neoprene is ineffective for everything, type EEEEEEENNNNNNN.

Leave your answer as string of ***14 capital letters.***

Solution:

NNNEENNEEEENEN

For nitrile gloves:

1) 70% nitric acid

Nitrile gloves fare poorly against concentrated nitric acid – the nitrile simply hydrolyses.

2) Dimethyl formamide

It is not effective — DMF is strongly hydrogen bonded to the nitrile groups of the gloves and therefore, as DMF solvates the nitrile group, it can cause the nitrile polymer chains in the glove material to swell, compromising structural integrity of the glove.

3) Furfural

It is not effective — furfural has an aldehyde group that can undergo the Knoevenagel condensation with nitriles, disrupting the polymer chain.

4) Linoleic acid

It is fairly effective against linoleic acid.

5) Perchloroethylene

It is also quite effective against perchloroethylene.

6) Phenol

It is not effective against phenol, because phenol reacts with the nitrile groups in the Pinner reaction, which can reduce the structural integrity of the glove, albeit at a slow rate. Combined with the hydrogen bonding mentioned in (2), this can wear out the glove quickly.

7) Propylene oxide

It is not effective against propylene oxide. Propylene oxide has a ring opening reaction.

For neoprene gloves:

1) 70% nitric acid

Neoprene gloves are quite effective against concentrated nitric acid.

2) Dimethyl formamide

Neoprene gloves are quite effective against DMF.

3) Furfural

Neoprene gloves are quite effective against furfural.

4) Linoleic acid

Neoprene gloves are quite effective against linoleic acid.

5) Perchloroethylene

It is not effective against perchloroethylene – the perchloroethylene interacts strongly with the polymer and causes it to swell, ruining the structural integrity of the polymer.

6) Phenol

It is effective against phenol.

7) Propylene oxide

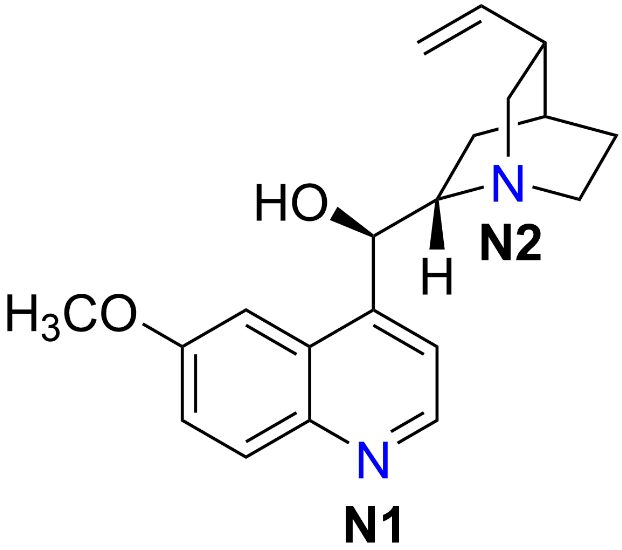
It is not effective against propylene oxide – it also undergoes a ring opening reaction.

Problem prepared by: Lim Dillion

AR46: Quinine

Malaria is a life-threatening disease caused by Plasmodium parasites that are transmitted to people through the bites of infected female Anopheles mosquitoes.

Historically, quinine was the most commonly used compound to treat malaria. The two nitrogen atoms in quinine are labelled **N1** and **N2** as shown below.



Which of the following statements are correct?

A) The lone pair of electrons on **N1** is found in the unhybridized 2p orbital of **N1**.
B) The lone pair of electrons on **N2** is found in the unhybridized 2p orbital of **N2**.
C) **N2** is more basic than **N1** as the lone pair of electrons in **N1** are closer to and more strongly attracted to its nucleus.
D) When shaken with deuterated water (D_2O), only one signal will disappear from the ^1H NMR spectrum of quinine.
E) In the ^1H NMR spectrum of quinine in TMS, apart from the signals that correspond to the quinoline aryl protons, there should theoretically be 16 other distinct signals.

*Leave your answer as a string of **capital letters** in ascending alphabetical order. For example, if A, B and D are correct, leave your answer as "ABD".*

Solution:

CD

A) The lone pair of electrons on **N1** is found in the unhybridized 2p orbital of **N1**.

False. The geometry around **N1** is trigonal planar, given the aromaticity of the arene group that it is a part of. Hence, the lone pair of electrons in **N1** is found in its $2sp^2$-hybridised orbital.

B) The lone pair of electrons on **N2** is found in the unhybridized 2p orbital of **N2**.

False. The geometry around **N2** is trigonal pyramidal, and there are no unhybridized 2p-orbitals in **N2**. Hence, the lone pair of electrons in **N2** is found in its $2sp^3$-hybridised orbital.

C) **N2** is more basic than **N1** as the lone pair of electrons in **N1** are closer to and more strongly attracted to its nucleus.

True. The lone pair of electrons in **N1** is in an sp^2-hybridised orbital whereas the lone pair of electrons in **N2** is in an sp^3-hybridised orbital. Due to increasing s-character, electrons in sp^2 orbitals are closer to and more strongly attracted by the nucleus and are therefore less available for protonation. Therefore, **N2** is more basic.

D) When shaken with deuterated water (D_2O), only one signal will disappear from the ^1H NMR spectrum of quinine.

True. Only the labile alcohol OH proton will undergo deuterium exchange. Since deuterium is NMR-inactive, only the signal corresponding to the OH group will disappear.

E) In the ^1H NMR spectrum of quinine in TMS, apart from the peaks that correspond to the quinoline aryl protons, there should theoretically be 16 other distinct peaks.

False. Apart from the 3 identical protons in the −OMe group in quinine, the rest of the protons are in different chemical environments and their signals should hence be, in theory, distinct. Since there are 24 H atoms in quinine and 5 of these protons are bonded to the quinoline aryl group, there should hence be $24 - 5 - (3 - 1) = \mathbf{17}$ distinct signals in the ^1H NMR spectrum of quinine.

Problem prepared by: Ranen Yong

AR47: What's Better Than Getting A Nobel Prize?

…Having your name immortalised as an element. While 954 individuals have received the Nobel Prize to date, only a select few will ever have the prestigious honour of having an element named after them.

How many elements are named after real people (past and present)?

Do not include elements only named indirectly after people (e.g. an element named after a lab, which in turn is named after a person, but no points for guessing what this element is!).

Solution:

13

Element number	Name of element	Person
96	Curium	Marie and Pierre Curie
99	Einsteinium	Albert Einstein
100	Fermium	Enrico Fermi
101	Mendelevium	Dmitri Mendeleev
102	Nobelium	Alfred Nobel
103	Lawrencium	Ernest Lawrence
104	Rutherfordium	Ernest Rutherford
106	Seaborgium	Glenn Seaborg
107	Bohrium	Niels Bohr
109	Meitnerium	Lise Meitner
111	Roentgenium	Wilhelm Roentgen
112	Copernicium	Nicolaus Copernicus
118	Oganesson	Yuri Oganessian

Problem prepared by: Lin Bohan

AR48: Lazy QA

Quinn is given five unlabelled samples and a list of five compounds:

1. $ZnSO_4$
2. $Al(NO_3)_3$
3. $CaCl_2$
4. KOH
5. $Fe(NO_3)_2$

Each sample is a solution containing one of the five compounds, and no two samples are the same. Quinn is given access to some common bench reagents and lab equipment:

Bench reagents	Lab equipment
• NaOH (aq) • NH_3 (aq) • $KMnO_4$ (aq) • KI (aq) • Dilute HNO_3 • Na_2CO_3 (aq) • $BaCl_2$ (aq) • $AgNO_3$ (aq)	• Nitrile gloves • Safety goggles • Bunsen burner, tripod and wire gauze • Lighter • Test tubes and rack • Test tube holder • Filter paper and funnel • Gas delivery tube and limewater • Crucible

Quinn is lazy and wishes to minimise the number of **bench reagents** he needs to use to identify all five samples.

Find the minimum number of bench reagents he can use to do so. For instance, if you believe he can identify the samples using only NaOH, NH_3 and $KMnO_4$, as well as all the lab equipment, input 3.

Hint: Do we need a positive test for all the compounds?

Solution:

1

… and that reagent is Na_2CO_3 (aq). Let's approach this question thoughtfully to see how we could arrive at such an answer.

One of the samples is KOH; we can't test for both its cation and anion. This means we should be identifying it by process of elimination (i.e, that we should get positive results for the other samples).

Of the compounds, $Al(NO_3)_3$ and $Fe(NO_3)_2$ can only be distinguished by testing for the cation since we are not given Al(s) to test for the nitrate anion. This means we could test for only the cations in the samples to minimise the number of reagents we need.

We could add NH_3 (aq) dropwise until in excess to differentiate Zn^{2+} (white ppt soluble in excess), Al^{3+} (white ppt insoluble in excess), and Fe^{2+} (green ppt insoluble in excess), but we need another reagent to differentiate Ca^{2+} and K^+ (such as NaOH (aq)). This means we need 2 reagents to identify the samples. Can we do better?

We recognise that Zn^{2+}, Al^{3+} and Ca^{2+} all yield white precipitates, if any, when we conduct cation tests since their compounds are white. Notice that Al^{3+} is the only acidic cation, so using a carbonate like Na_2CO_3 gives us a white ppt of $Al(OH)_3$ and effervescence of CO_2 gas, which we can positively identify using limewater. Following this path, Fe^{2+} gives a green ppt of $FeCO_3$ (which can oxidise in air to reddish-brown $Fe(OH)_3$); Ca^{2+} and Zn^{2+} both yield white precipitates of $CaCO_3$ and $ZnCO_3$ respectively.

There is actually a way to distinguish both carbonates, using the fact that ZnO is thermochromic and turns yellow when heated. The precipitates can be filtered out and placed in the crucible to be heated; once the CO_2 is driven off, we are left with white CaO and yellow ZnO.

K^+ will be the only sample to not have a precipitate form.

These compounds can therefore be distinguished using only Na_2CO_3 (aq) and the lab equipment provided!

Problem prepared by: Lie Huan Yew

AR49: Nitrous Engine

A mechanic builds an experimental car engine that, instead of running on gasoline and air, runs on nitrous oxide (N_2O) and nitromethane (CH_3NO_2). The engine works as follows:

1. Nitrous oxide and nitromethane are mixed in a specific ratio. This ratio may or may not be stoichiometric.
2. All the nitrous oxide decomposes into its elements.
3. Nitromethane combusts according to the following equation:

$$4\ CH_3NO_2 + 3\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O + 2\ N_2$$

4. The hot exhaust gases (including water vapour) leave the engine.

A 10.0 g sample of the exhaust gas is collected, containing no nitromethane. It was cooled to room temperature and passed through NaOH (aq). 5.97 g of gas remained, and this remaining gas was able to relight a glowing splint.

Determine the percentage by mass of nitrous oxide in the initial mixture.

Leave your answer to 3 significant figures. Omit the % sign.

Solution:

65.4

The 10.0 g of exhaust must have come from the **same** mass of N_2O and CH_3NO_2. Let the mass of N_2O in this mixture be x g. Using atomic masses from the data sheet,

$$nN_2O = \frac{x}{44.02}\text{ mol}$$
$$nCH_3NO_2 = \frac{10-x}{61.044}\text{ mol}$$

All the O_2 required for combustion must have come from the decomposition of N_2O. The reactions that occur are:

$$2\ N_2O \rightarrow 2\ N_2 + O_2$$

$$4\ CH_3NO_2 + 3\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O + 2\ N_2$$

Because there was no CH_3NO_2 in the exhaust, all of it must have combusted, which means O_2 was in stoichiometric excess (confirmed by the glowing splint test). The exhaust gases are CO_2, H_2O, N_2 and O_2. After cooling to room temperature and passing through NaOH (aq), only N_2 and O_2 will remain.

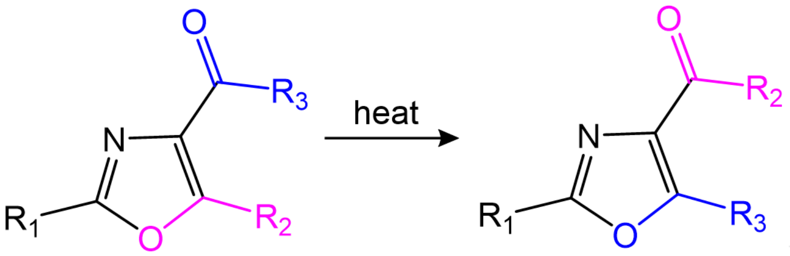
$$\text{Amount of } O_2 \text{ from decomp. of } N_2O = \frac{1}{2} \times \frac{x}{44.02} = \frac{x}{88.04}\text{ mol}$$
$$\text{Amount of } O_2 \text{ required for combustion of } CH_3NO_2 = \frac{3}{4} \times \frac{10-x}{61.044} = \frac{30-3x}{244.176}\text{ mol}$$
$$\text{Amount of excess } O_2 = \frac{x}{88.04} - \frac{30-3x}{244.176}\text{ mol}$$
$$\text{Amount of } N_2 \text{ produced} = \frac{x}{44.02} + \frac{2}{4} \times \frac{10-x}{61.044} = \frac{x}{44.02} + \frac{10-x}{122.088}\text{ mol}$$
$$\text{Mass of } N_2 \text{ and } O_2 \text{ in exhaust} = 32\left(\frac{x}{88.04} - \frac{30-3x}{244.176}\right) + 28.02\left(\frac{x}{44.02} + \frac{10-x}{122.088}\right)$$
$$= 0.36347x - 3.93159 + 0.39316x + 0.63653x + 2.29507 - 0.22951x$$
$$= 1.16365x - 1.63652 = 5.97$$
$$x = 6.53678$$

$$\text{Hence percentage mass of } N_2O = \frac{6.53678}{10.0} \times 100 \approx \mathbf{65.4}\ \%$$

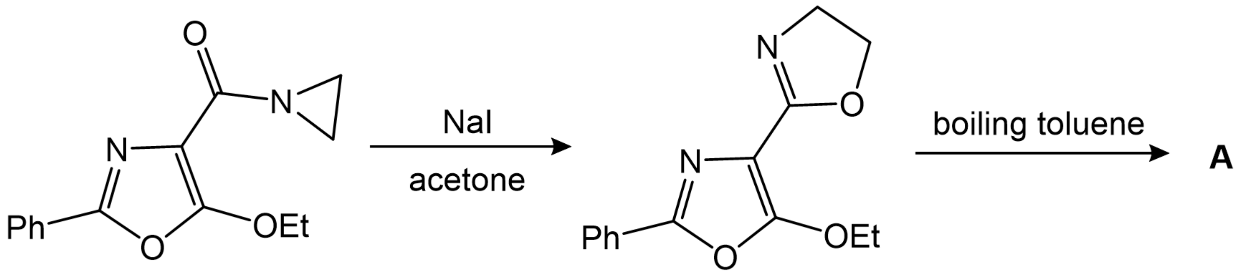
Problem prepared by: Wang Jiahua

AR50: What's The Difference?

The Cornforth rearrangement was first reported in 1949, and is named after chemist John Cornforth. It is a reaction typically used in the synthesis of amino acids. The thermal rearrangement of a 4-carbonyl substituted oxazole is shown below:

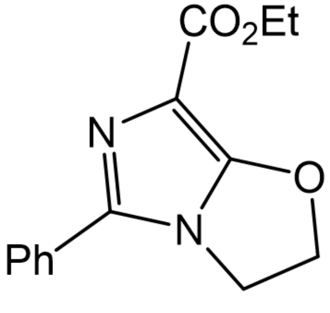


What is the structure of compound A in the synthesis below?



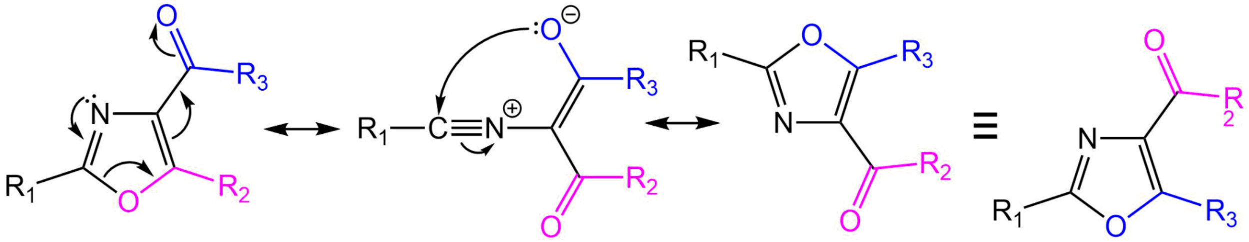
Leave your answer as an organic structure.

Solution:



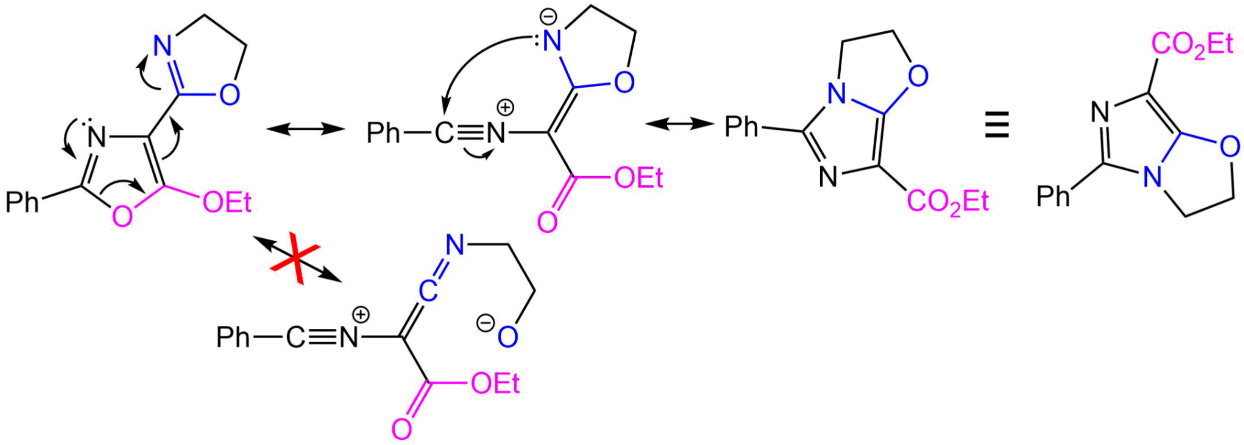
A

The mechanism of the Cornforth rearrangement is shown below.



A pericyclic ring opening first takes place which results in a nitrile intermediate. This then undergoes rearrangement to the oxazole which is isomeric to the starting one.

We may use the same mechanism to determine the structure of **A**:



Note that the electrons are pushed to the nitrogen atom rather than the oxygen atom, as the imine intermediate formed in the latter is more unstable (the first intermediate has multiple resonance structures that disperse the negative charge on the N atom).

Problem prepared by: Lie Huan Yew