W-⌇-CC | CODS
WINTER CHEMISTRY OLYMPIAD

TEAM NAME	ANSWER KEY
DATE	
PROCTOR'S NAME	
CIN	

Cleaving Bonds (Free Response)

January 25 11 am EDT, 2025
Maximum: 1 hour 30 minutes

Additional Materials: PEC Packet or USNCO Data Sheet

READ THESE INSTRUCTIONS FIRST

Write your name, date, CIN, and your proctor's name in the spaces at the top of this page.

This examination has **12 problems**. You may solve the problems in any order.
You will have **1 hour 30 minutes** to solve all the problems.

Write your answers in the appropriate answer boxes provided.
Read the instructions on the submission website very carefully.

During the round, at any time the round will be **"catalyzed" for 2 × 15 minutes**. When catalyzed, **double points are given for all questions** answered correctly during the period! As a team, consider which questions to save until then.

You must stop working when the **STOP** command is given. Failure to stop writing will lead to the nullification of your examination.

The use of an approved, non-programmable scientific calculator is expected, where appropriate.
The number of marks is given in the table at the top of each question.

This document consists of **33** printed pages.

Problems & Grading Information

	Title	Author(s)	Total score
1	Operation (Chalco)Pyrite	Vincent Yap	4
2	Minecraft	Pin-Jui Lin	4
3	Minecraft Furnace	Vincent Yap	4
4	MUSTARDDDDDDDDDDDDDDD	Bach Hoang	4
5	this is one lengthy reference to J. Cole's "Grippy"	Bach Hoang	8
6	Oh no! It's Sparkle!	Pin-Jui Lin	8
7	Can you save the Penacony?	Pin-Jui Lin	8
8	Back to the basics…	Dillion Lim	8
9	Hi! It's Sparkle again!	Pin-Jui Lin	16
10	Complex Complexes	Gerardo Y. Angeles	16
11	原來你也玩崩壞星穹鐵道 (Oh, you play Honkai: Star Rail too)	Pin-Jui Lin	16
12	Doxycycline	Ranen Yong	16
		Raw Total	112

Authors:

- Bach Hoang, United States
- Dillion Lim, Singapore
- Gerardo Y. Angeles, Mexico
- Pin-Jui Lin, Taiwan
- Ranen Yong, Singapore
- Vincent Yap, Singapore

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- Ranen Yong, Singapore

Operation CC#1	Stage	1.1	1.2	1.3	Bonus	Total
	Risk Level	1	1	1	1	4

Problem 1: Operation (Chalco)Pyrite

by Dr. ChillySaus, Pyrite Gorge, Terra

"Silver and gold…

…won't save my rotting soul"

Chalcopyrite is an ore with great economic value. Its name arises from *chalco-* (meaning copper), and pyrite (FeS_2), also known as fool's gold.

1.1 The %mass of copper in chalcopyrite is 34.62%. Suggest the chemical formula of chalcopyrite.

> $CuFeS_2$
> Also accept $FeCuS_2$ obviously…

Chalcopyrite is first heated at around 600℃ with oxygen to form copper sulphate, haematite and an acrid gas.

1.2 How many equivalents of oxygen are consumed per mole of chalcopyrite? Give your answer as an integer/decimal.

> $4CuFeS_2 + 15O_2 \rightarrow 4CuSO_4 + 2Fe_2O_3 + 4SO_2$
> **15/4 O_2 = 3.75 O_2**
>
> Where we're from, O-level students must know what haematite is. Too bad.

1.3 Quicklime (CaO) is also added during the heating process. Which of these reactions are **not** representative of quicklime's role in the melt?

a) $CaO + SO_2 \rightarrow 2CaSO_3$
b) $CaSO_3 + \frac{1}{2} O_2 \rightarrow CaSO_4$
c) $\mathbf{CaO + Fe_2O_3 \rightarrow CaFe_2O_4}$
d) $CaO + SiO_2 \rightarrow CaSiO_3$

Congratulations, Doctor. Here's a medal for your hard work.

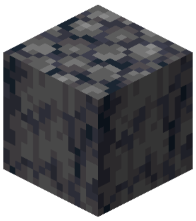
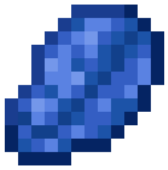
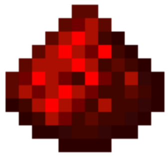
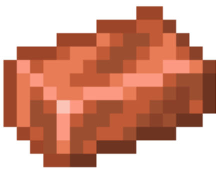
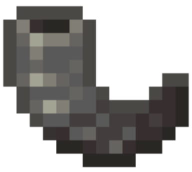
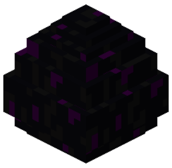
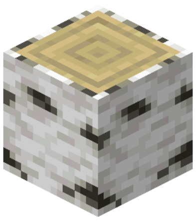
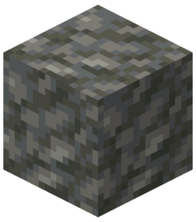
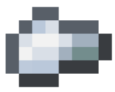
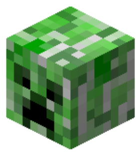
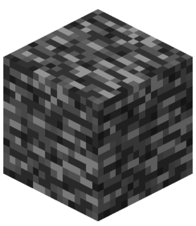
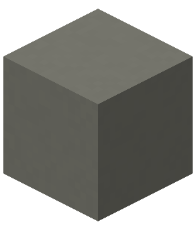
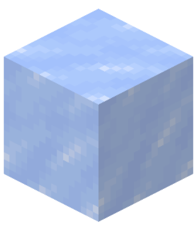
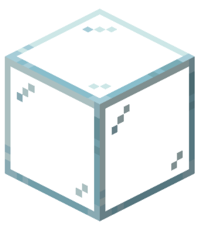
Problem 2	Question	2.1	2.2	2.3	Bonus	Total
	Points	1	1	1	1	4

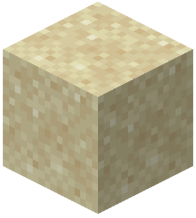
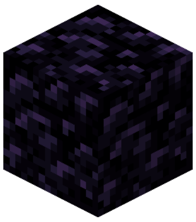
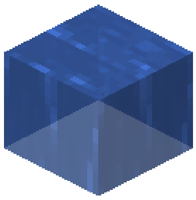
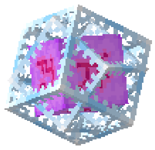
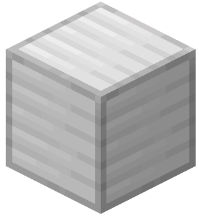
Problem 2: Minecraft (bronze, analytical)

by Pin-Jui Lin (nightlight_1201), Taiwan

In geology and mineralogy, a mineral or mineral species is, broadly speaking, a solid substance with a well-defined chemical composition and a specific crystal structure that occurs naturally in pure form.

2.1 **Which** of the following are minerals that exist in the real world?

				
A. quartz	B. basalt	C. lazurite	D. red stone	E. amethyst
				
F. native copper	G. goat horn	H. dragon egg	I. gold	J. nether star
				
K. birch log	L. tuff	M. calcite	N. native iron	O.creeper head
				

P. bedrock	Q. concrete	R. ice	S. glass	T. diamond
				
U. sand	V. obsidian	W. water	X. end crystal	Y. iron block

minecraft (acefimnrt)
Remarks: Ice is a mineral, as it naturally forms inorganic crystals. Native iron is naturally formed, but humans fabricate the iron block. Lapis lazuli is not a mineral, but lazurite is a mineral.

One day, while mining in a large cave, Steve discovered a mysterious ore and collected four blocks of it, weighing 9.04 tons. Curiously, he crushed the ore into a fine powder using his bare fists. He then heated the powdered ore with coal in a furnace, producing a liquid metal layer. This molten metal, weighing 3.14 tons, was drained into his aquarium to cool. Once cooled, Steve dissolved the metal in concentrated nitric acid, leaving behind 0.69 tons of insoluble metal **X**, while the solution contained two types of metal ions, **A** and **B**. Next, he electrolyzed the solution using metal **Z** as the anode and a carbon plate as the cathode. After electrolysis, the solution no longer contained metal ions **A** and **B** but only metal ions **C,** which has the same number of protons as metal ion **B**. The solution was then filtered to recover 2.14 tons of insoluble metal **Y.** The solution was subsequently boiled to dryness and roasted in air, forming a binary compound **D**. Steve smelted the binary compound **D** with coal, yielding 2.45 tons of Metal **Z.**

2.2 It is known that the mysterious ore only contains minerals from the problem above. <u>**Identify**</u> metal ions **A, B**, and **C**, binary compound **D**, and metals **X, Y**, and **Z.** (Express in the format of A/B/C/D/X/Y/Z; for example, if A is Zn^{2+} and B is Sc^{3+}, write Zn2+/Sc3+/…)

Cu2+/Fe3+/Fe2+/Fe2O3/Au/Cu/Fe
A = Cu^{2+}, B = Fe^{3+}, C = Fe^{2+}, D = Fe_2O_3, X = Au, Y = Cu, and Z = Fe.

2.3 Calculate the mass percentage of metal **Z** in the ore**.**

$$\frac{3.14 - 0.69 - 2.14}{9.04} = \boxed{3.43\%}$$

Problem 3	Question	3.1	3.2	3.3	Bonus	Total
	Points	1	1	1	1	4

Problem 3: minecraft furnace

by ChillySaus (Java edition), Singapore

For this question, assume that the ΔH (and ΔS) of a reaction do not change with temperature, even though we know that's not really true.

An Ellingham diagram is used by metallurgists to determine if extracting metals are feasible across different temperatures. The different lines indicate the ΔG of **oxidation** across various metals (and carbon) at varying temperatures.

3.1 Which **thermodynamic variable** does the **gradient of each line** in the Ellingham diagram represent?

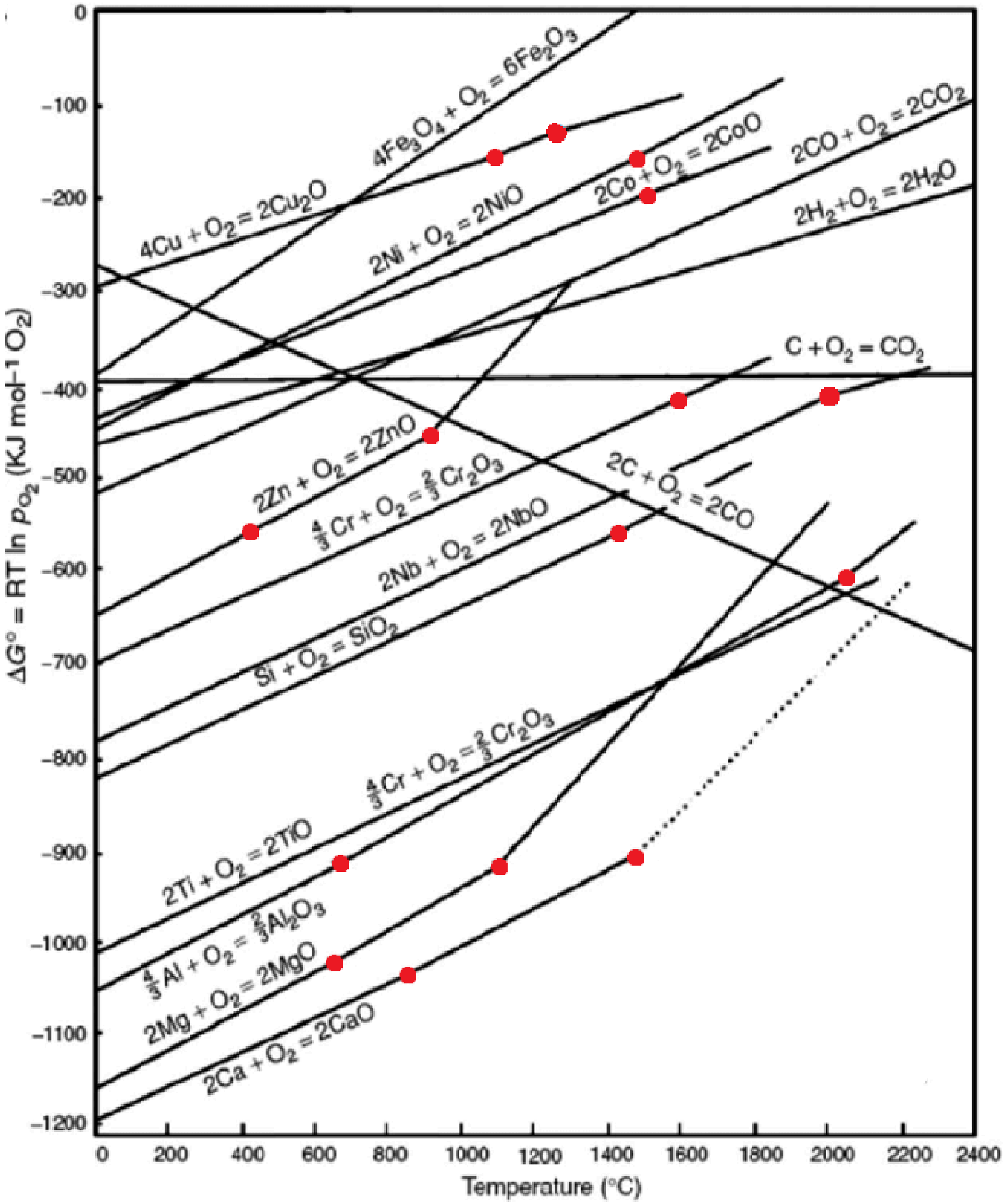
a) ΔH
b) −ΔH
c) ΔS
d) −**ΔS**

3.2 At what temperature can the carbothermal reduction of zinc oxide start to proceed? Give your answer to the nearest 100 Celcius.

1000

3.3 The lines in the Ellingham diagram **change their gradient** at the coloured nodes. Why does the gradient get steeper after each node? The nodes represent:

a) melting and boiling points of the elements
b) **melting and boiling points of the oxides**
c) decomposition temperatures of the oxides
d) reaction change in spontaneity



0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
-1100
-1200
ΔG° = RT ln p_{O_2} (KJ mol^{-1} O_2)
$4Fe_3O_4 + O_2 = 6Fe_2O_3$
$4Cu + O_2 = 2Cu_2O$
$2Ni + O_2 = 2NiO$
$2Co + O_2 = 2CoO$
$2CO + O_2 = 2CO_2$
$2H_2 + O_2 = 2H_2O$
$C + O_2 = CO_2$
$2Zn + O_2 = 2ZnO$
$\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$
$2C + O_2 = 2CO$
$2Nb + O_2 = 2NbO$
$Si + O_2 = SiO_2$
$\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$
$2Ti + O_2 = 2TiO$
$\frac{4}{3}Al + O_2 = \frac{2}{3}Al_2O_3$
$2Mg + O_2 = 2MgO$
$2Ca + O_2 = 2CaO$
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Temperature (°C)

Problem 4	Question	4.1	4.2	4.3	Bonus	Total
	Points	1	1	1	1	4

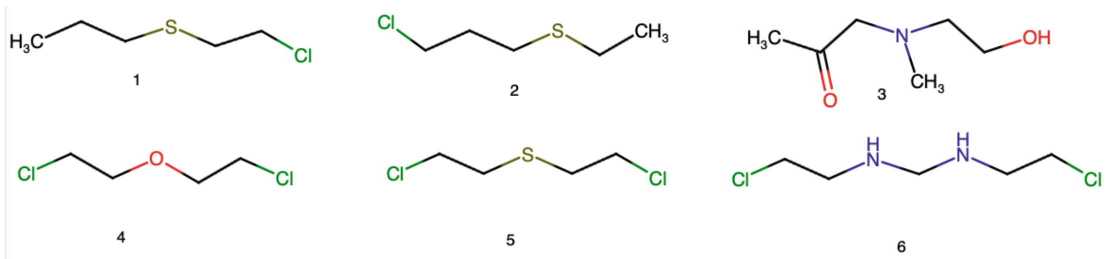
Problem 4: MUSTARDDDDDDDDDDDDDDD

by Bach Hoang, United States

MUSTARDDDDDDDDDDDDDDD - Kendrick Lamar, *tv off*

Mustard gas is a carcinogen and a mutagenic alkylating agent used in World War 1 and World War 2. In the wider sense, compounds with the structural element **B**C_2H_4X, where **X** is any leaving group and **B** is a Lewis base, are known as *mustards.* The most common type of mustard gas, codenamed **H**, is synthesized by reacting dry ethylene and disulfur dichloride under controlled conditions.

4.1 **Which** one of these compounds are considered mustards? **Which** one of these compounds is **H**?



1, 4, 5, 6 are mustards; 5 is H.

4.2 **What** molecule(s) in the human body does mustard gas interact with that causes its adverse effects? **Which** functional group allows this molecule(s) to interact?

DNA's amine groups

4.3 **H** is normally colorless, but when used in war, it has a distinct yellow color. **Explain** why this is the case.

The synthesis process of "H" involves chlorine gas - which is not fully reacted, causing the yellow color.

Problem 5	Question	5.1	5.2	5.3	Bonus	Total
	Points	2	2	2	2	8

Problem 5: this is one lengthy reference to J. Cole's "Grippy"

by Bach Hoang, United States

It's…It's…It's…

In this problem, we are going to investigate "grippy powders" - these are "grippy" as they are used to absorb sweat from rock climbers and badminton players' hands, allowing them to have a better grip.

To prepare the principal compound in "grippy powders" in laboratories, you can't directly react Na2CO3 with a soluble salt of the metal to precipitate the compound - as that would create a hydrated complex. The mass percentage of carbon and hydrogen in this complex is 9.89% and 2.2%, respectively.

5.1 **Determine** the compound present in the "grippy powder" and the hydrated compound.

(mg4(co3)3oh2.3h2o)

…Believe it or not like Ripley's…

5.2 Here are 10 facts about random elements and compounds. Are they **true or false**? If true, provide a short explanation – if false, provide one exception.
Author's note: the explanation is only half the grade!

1. At room temperature (298K), in the first 103 elements, there are only two elements (Hg, Br) that exist in liquid form.
2. An element can present 12 oxidation states in compounds.
3. Finely powdered magnesium reacts to water - the reaction proceeds the same way as calcium and barium.
4. Technetium is the only element that is not stable and is both preceded and followed by elements with stable form.
5. White phosphor exhibits phosphorescence.
6. Adding base to a solution with lead (II) nitrate creates the related hydroxide.
7. Radical species exist in nature.
8. Quintuple bonds (bonds with 10 electrons) exist in chemical compounds.
9. Vitriol is the general chemical name encompassing a class of chemical compounds comprising sulfates of certain metals – originally, iron or copper - so all compounds containing "vitriol" in its archaic name are inorganic.

10. High-temperature superconductors (e.g: YBCO) require rare-earth elements in it to be superconductive.

…I was thinking "damn, your whole clique bad"..

1: F (francium);
2: T (-3 to +9 bar -2, by iridium),
3: F (does react but not the same way as Ca / Ba)
4. F (prometheum),
5: F (chemiluminescence not phosphorescence);
6: F (creates hydrated nitrate instead)
7: T (O2)
8: T there are compounds trust
9: F (sweet oil of vitriol is diethyl ether)
10: F (bscco)

5.3 In this problem, 16 inorganic compounds are listed here – your task is to **arrange** them into four groups that share a common thread. This thread may be chemical, historical, applied, or something else….

$AgNO_3$	CrO_3	$GaBr_3$	$GeBr_4$
H_2O_2	KHF_2	KI_3	$KMnO_4$
KO_2	KrF_2	NaN_3	Na_2O_2
OsO_4	$RuCl_3$	$ScCl_3$	TcF_6

OsO4	KMnO4	ScCl3	KI3
AgNO3	H2O2	GaBr3	KHF2
RuCl3	KO2	TcF6	KrF2
CrO3	Na2O2	GeBr4	NaN3

yellow: oxidation reagents used in organic synthesis
cyan: used to create oxygen in various use cases
purple: halogenic salts of elements predicted by Mendeleev's works on the periodic table
green: compounds that contain a 3c-4e bond

Problem 6	Question	6.1	6.2	6.3	Bonus	Total
	Points	2	2	2	2	8

Problem 6: Oh no! It’s Sparkle! (silver, analytical)

by Pin-Jui Lin (nightlight_1201), Taiwan

You finally board the airship, awaiting the Charmony Festival's commencement. Yet, Sparkle's sudden entrance breaks the festive atmosphere. That laughter-worshiping girl had 999 bombs on the airship... seriously, how on earth did she get her hands on so many weapons of mass destruction? But in any case, you are duty-bound to stand up and protect the airship. It is known that the majority of bombs are fake, and only a few are real; hence, you need a way to identify the explosive quickly.

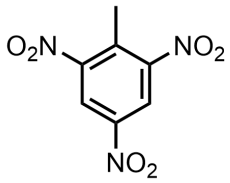
After gathering all 999 bombs, you find Miss Sparkle thoughtfully marking 214 bombs as inorganic. You then decided to take samples from each bomb and run the following colorimetric test to determine which bombs were real.

▲ An image of a bomb

- **Chlorate**: Mix 1 ml of the dilute indigo carmine solution with 5 ml of concentrated hydrochloric acid, and the mixture is heated to boiling. 5 ml of the sample is added to this boiling mixture. If chlorate is present, the solution turns from blue to __**A**__.
- **Nitrate**: Add a drop of sulfanilic acid and α-naphthylamine, then add a small amount of powdered zinc. The addition of the zinc reduced the nitrate to **X**, and the **X** reacted with sulfanilic acid to produce **Y** and reacted with the α-naphthylamine to create the red compound.
- **Perchlorate**: A drop of 0.3% solution of Methylene is put into a sample. The methylene blue will form an insoluble purple precipitate if perchlorate is present.
- **Ammonium**: Combining potassium hydroxide and potassium iodide with mercuric chloride or mercury iodide produces a complex **Z.** When ammonia is present, it produces a dirty brown precipitate $HgO{\cdot}Hg(NH_2)Cl$.

6.1 **Identify** the color **A** and substance **X, Y,** and **Z.** Provide your answer in the format A/X/Y/Z (e.g., neon-pink/Sc3+/ScCl3/MgO). Both the name and the chemical formula are acceptable.

Colorless / Nitrite (NO_2^-) or Nitrous Acid (HNO_2) / Diazobenzenesulfonic Acid ($C_6H_4N_2O_3S$) / Potassium Tetraiodomercurate(II) ($K_2[HgI_4]$) or potassium aquatriiodomercurate(II) $K[Hg(H_2O)I_3]$



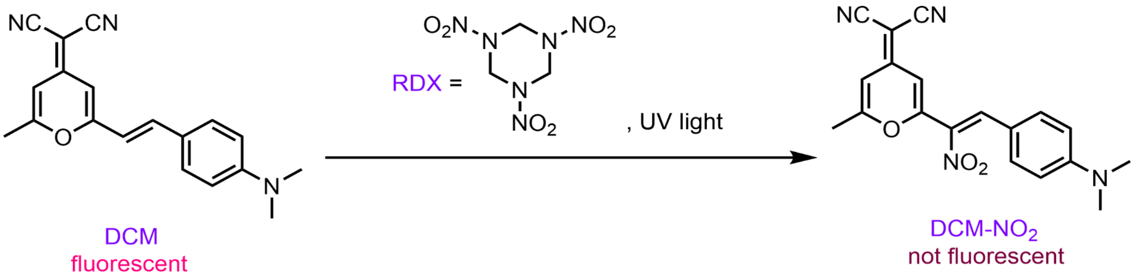
Among the rest of the bombs, Robin finds that Sparkle has labeled 451 bombs as TNT, or 2,4,6-trinitrotoluene. Now, you need to come up with a way to differentiate TNT from other chemicals.

6.2 **<u>Propose</u>** a chemical method to detect TNT and **<u>explain</u>** how this method works. You may use any chemical reaction to perform the test, but direct measurement techniques such as NMR, MS, or IR are not allowed. The method should rely on observable chemical changes, such as color formation, gas emission, precipitation, or fluorescence. The test itself doesn't need to be 100% accurate; for example, if the question asks you to detect chloride ions, adding silver nitrate to observe white precipitation is a good answer despite silver sulfite also being a white precipitate.

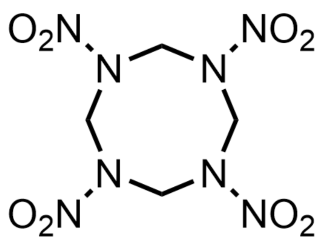
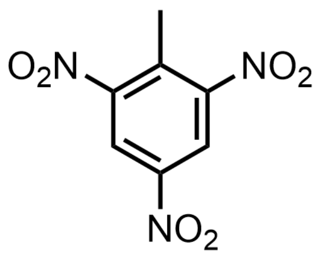
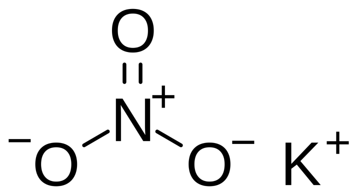
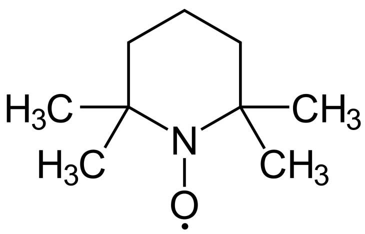
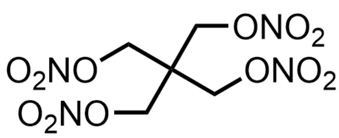
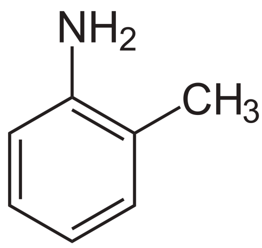
Any sensible method is accepted, for example:

- TNT can be detected colorimetrically by forming a colored Meisenheimer complex in a highly alkaline solution (e.g., with KOH). (TNT is pH indicator)
- Reducing TNT to an aromatic amine with Sn allows detection via the Ehrlich test, where the amine reacts with p-dimethylaminobenzaldehyde to form a colored imine.
- Alternatively, the reduced amine can undergo azo coupling with another aryl amine to produce a colored azo dye.
- TNT is electron-deficient and can quench the fluorescence of electron-rich fluorophores through photo-induced electron transfer (PET). This occurs when the excited fluorophore donates an electron to TNT, leading to fluorescence suppression, which can be used to detect TNT.
- Put primary explosives like silver azide or nitroglycerin to see if the compound detonates.

Black Swan discovers that Sparkle has labeled 333 bombs as containing RDX, the explosive agent in C4 plastic explosives. To quickly identify which bombs contain RDX, you decide to construct a fluorescence sensor with DCM as the fluorescent molecule. When exposed to UV light, RDX interacts with DCM, leading to fluorescence quenching.



6.3 <u>**Which**</u> of the following molecules can also be detected using DCM and UV light?

		
A. HMX	**B**. TNT	**C**. potassium nitrate
		
D. TEMPO	**E**. PETN	**F**. o-toluidine

A and **E**, because the fluorescence of the DCM dye is quenched after its reaction with $NO_2\cdot$ or NO_2^+.

“214 inorganic bombs, 451 TNT bombs, 333 RDX bombs…. Wait! That’s only 998 bombs. What about this final bomb!?” March 7th shouted. Indeed, there’s one bomb left, with its eyes glowing red. You investigate this bomb closely, only to find out that there’s a piece of paper stuffed inside the bell. What! Antimatter bomb!? Well… good luck dealing with that one.

Problem 7

Question	7.1	7.2	7.3	Bonus	Total
Points	2	2	2	2	8

Problem 7: Can you save the Penacony? (silver, physical)

by Pin-Jui Lin (nightlight_1201), Taiwan

To save the airship from Sparkle's hand, you're tasked with identifying and diffusing 999 bombs. Now, with only one bomb left, the antimatter bomb, you inform the group chat immediately.

7.1 <u>**Write**</u> the chemical equation for the decay of oxygen-15.

Oxygen-15 -> nitrogen-15 + position + neutrino + gamma ray

$$ {}^{15}_{8}\mathrm{O} \longrightarrow {}^{15}_{7}\mathrm{N} + \mathrm{e}^{+} + \nu_e + \gamma \qquad \text{(nuclide only)} $$

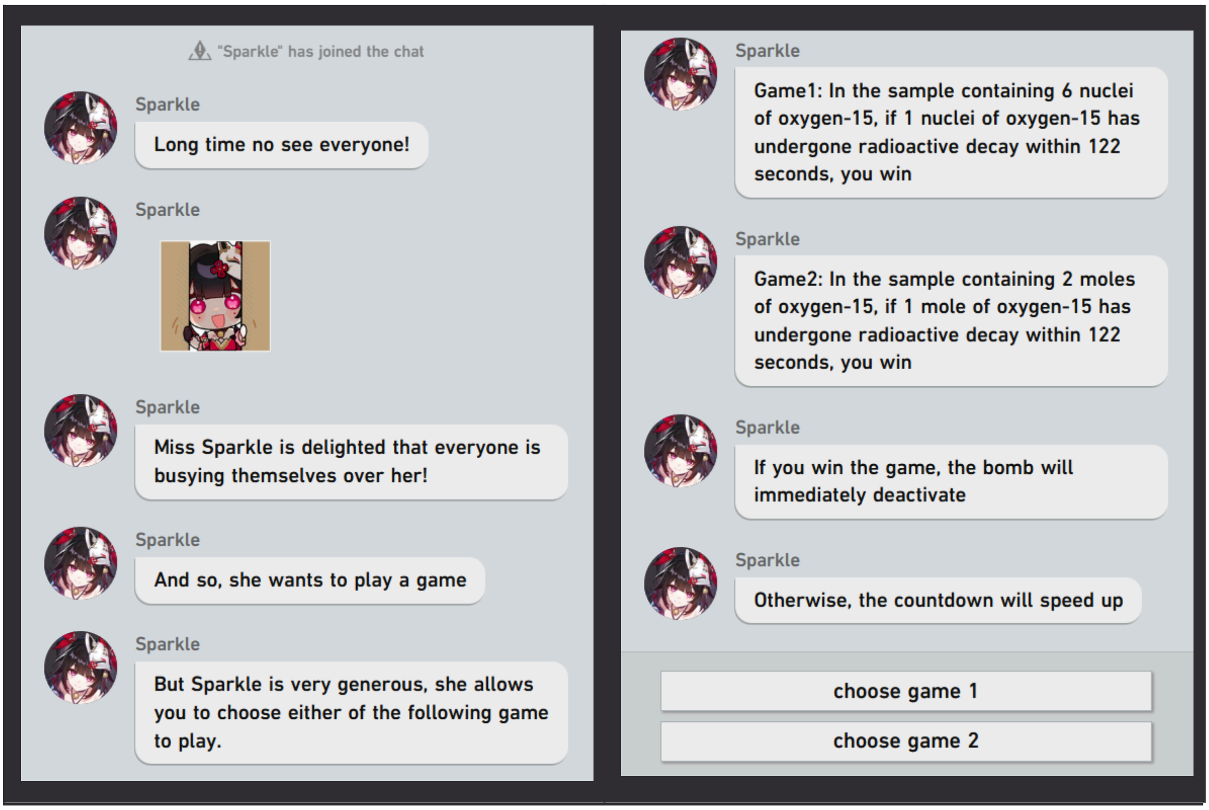
$$ {}^{15}_{8}\mathrm{O} \longrightarrow {}^{15}_{7}\mathrm{N}^{-} + \mathrm{e}^{+} + \nu_e + \gamma \qquad \text{(entire atom)} $$

7.2 <u>**Determine**</u> the time it takes for a bomb to explode, assuming the bomb is a closed system, and the process is isothermal.

$$ t_{1/2} = \frac{\ln 2}{k} = 122 \implies k = 5.682 \cdot 10^{-3} $$

$$ \ln[A] = \ln[A]_0 - kt $$

$$ \implies \ln 0.2 = \ln 32 - 5.682 \cdot 10^{-3} t \implies \boxed{t = 893\ \mathrm{s}} $$



7.3 <u>**Which**</u> game has a higher chance of winning? Briefly <u>**explain**</u> why.

Game 1, the likelihood of getting exactly half of the nuclei to decay is extremely small as the number of particles increases. Also, one mole is an aggregate of exactly

$6.02214076 \times 10^{23}$ elementary entities.

Well, you did increase the chance of surviving, but that doesn’t mean you successfully defused the bomb. Did you save the airship? Or is it the prank all along?
Penacony Final Cinematic Cutscene Honkai Star Rail 2.3

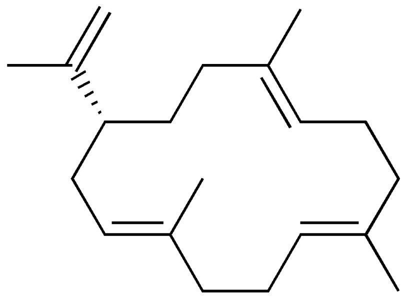
Problem 8	Question	8-1	8-2	8-3	Bonus	Total
	Points	2	2	2	2	8

Problem 8: Back to the basics...

by Dillion Lim (theorangejuice), Singapore

One of the first things organic chemistry students learn is the idea of isomerism, and with it, the concept of stereoisomerism. Take a moment to recall what enantiomers and diastereomers are.

Cembrene A is a trail pheromone for termites. Its structure is shown below, a fairly basic skeleton structure.

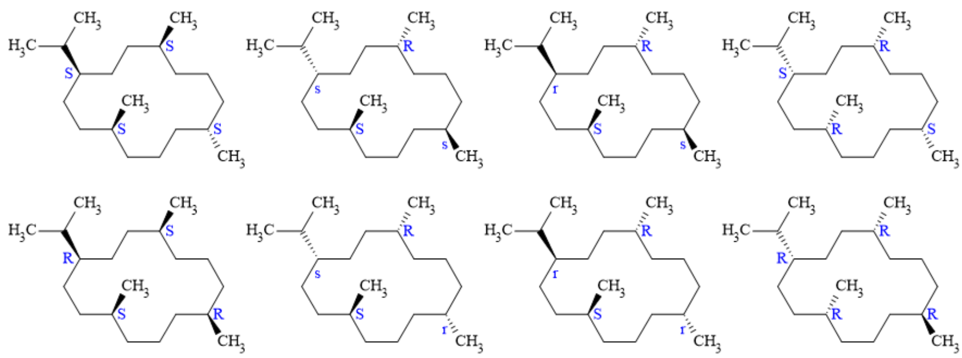


Cembrene A was passed over excess hydrogen gas over a platinum catalyst.

8.1 <u>**How**</u> many potential chiral centers can be formed in the reaction?

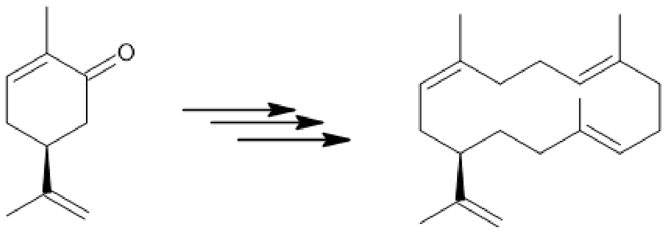
4, see below for the 4 potential chiral centers (2 are either chiral or psuedochiral).

8.2 <u>**How**</u> many stereoisomers of the hydrogenated product are there?



There are 8 stereoisomers, not 2^4 = 16 because there are 2 pseudochiral centers!

The total synthesis of cembrene A has the following precursor:



There are 5 steps in the synthesis, and 4 intermediates. They are:

1) KH, THF, rt

1

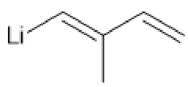
1) Ac_2O
2) Li, $EtNH_2$
3) AcOMs, rt

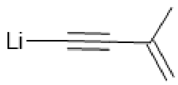
2

1) H^+, MeOH

3

1) LDA, TfCl

2) 

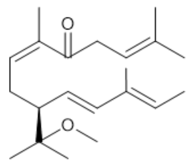
3) 

4) $LiAlH_4$

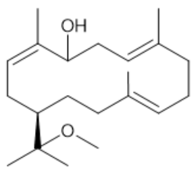
4

1) $NaBH_4$, $CeCl_3$
2) H_2, PtO_2

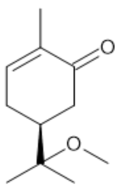
5



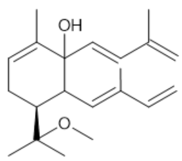
A



B

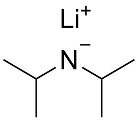


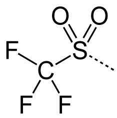
C



D

8.3 **<u>Assign</u>** the steps and intermediates in order. If the precursor, followed by step **1** leads to intermediate **A**, followed by step 2 leads to intermediate **B**, and so on, then write your answer as **1A2B3C4D5**. The last step should lead to the final product, cembrene A.

[LDA is 

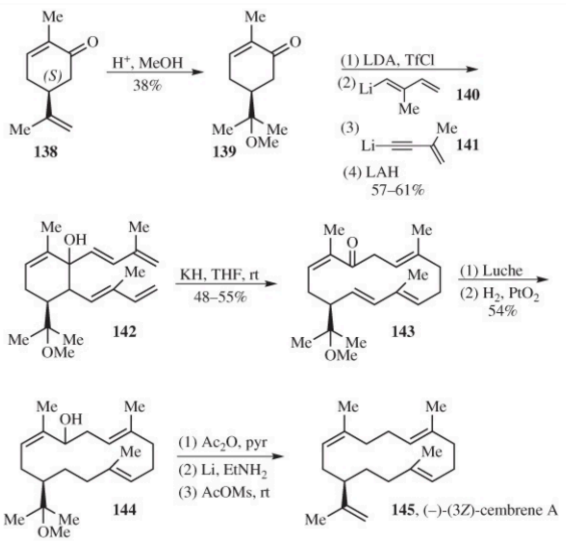
; Tf is 

; Ms is CH_3SO_2-; Ac is CH_3C=O]

3C4D1A5B2.

The full scheme is shown on the right.

The answer can be gotten by doing a series of eliminations and educated guesses. For example, the simplest product should be the first intermediate, and since there is a luche reduction in the middle, the ketone must come before the alcohol group.



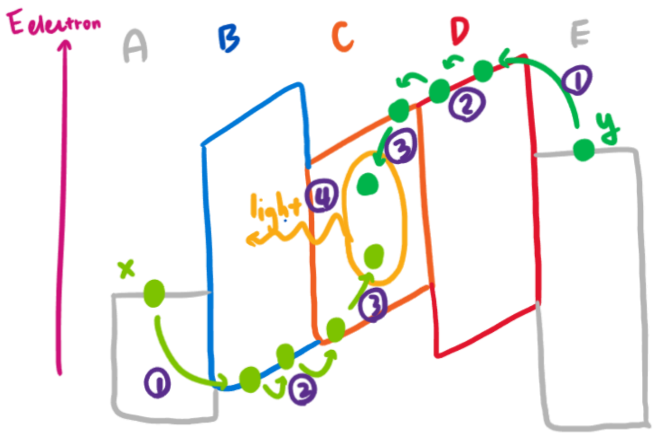
Problem 9	Question	9.1	9.2	9.3	Bonus	Total
	Points	4	4	4	4	16

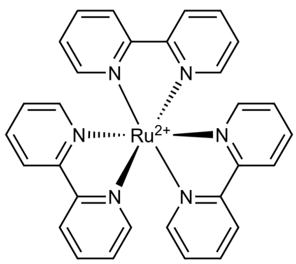
Problem 9: Hi! It's Sparkle again! (gold, inorganic)

by Pin-Jui Lin (nightlight_1201), Taiwan

When Sparkle made the bomb, she made the red glowing eye out of an organic light-emitting diode (OLED), which she synthesized and manufactured herself. She spent hours in her lab perfecting the process, ensuring the OLED emitted the exact eerie red light she envisioned. But first, she needs to brush up on how OLED works.

An OLED consists of several layers of thin films of organic materials sandwiched between two electrodes. When voltage is applied, **(A)electrons** and **(B)holes** are injected from the **(C)cathode** and **(D)anode** through a process known as **(Q)carrier injection. (A)electrons** drift through **(E)electron transport layer(ETL)**, while **(B)holes** drift through **(F)hole transport layer(HTL)**; these drifts are called **(R)carrier transportation.** When electrons and holes move into the **(G)emission layer(EML),** they **(S)generate an exciton**, which, in turn, **(T)decays radiatively** to produce light.





For example, If the Ru^{2+} complex to the left is used as the active substance, it is reduced at the cathode to **X**, acting as a **(M)electron/hole** carrier. It is also oxidized at the anode to **Y**, acting as a **(N)electron/hole** carrier. Radiative decay occurs when an electron hops from **X** to **Y** via a comproportionation reaction to create a ground-state Ru^{2+} complex and an excited-state ion Ru^{2+} complex. The excited complex decays to the ground state through phosphorescence, emitting light (red-orange, λ = 630 nm).

9.1 **Identify** the labels in the figure for substances **A** to **G** (choose from ABCDExy) and processes **Q** to **T** (choose from 1234). Additionally, **determine** the roles of substances **M** and **N** (electron or hole) and ions **X** and **Y**. Provide your answer in the format A/B/C/D/E/F/G/Q/R/S/T/M/N/X/Y; for example, if **X** is Zn^{2+} and **Y** is Sc^{3+}, write …/Zn2+/Sc3+/)

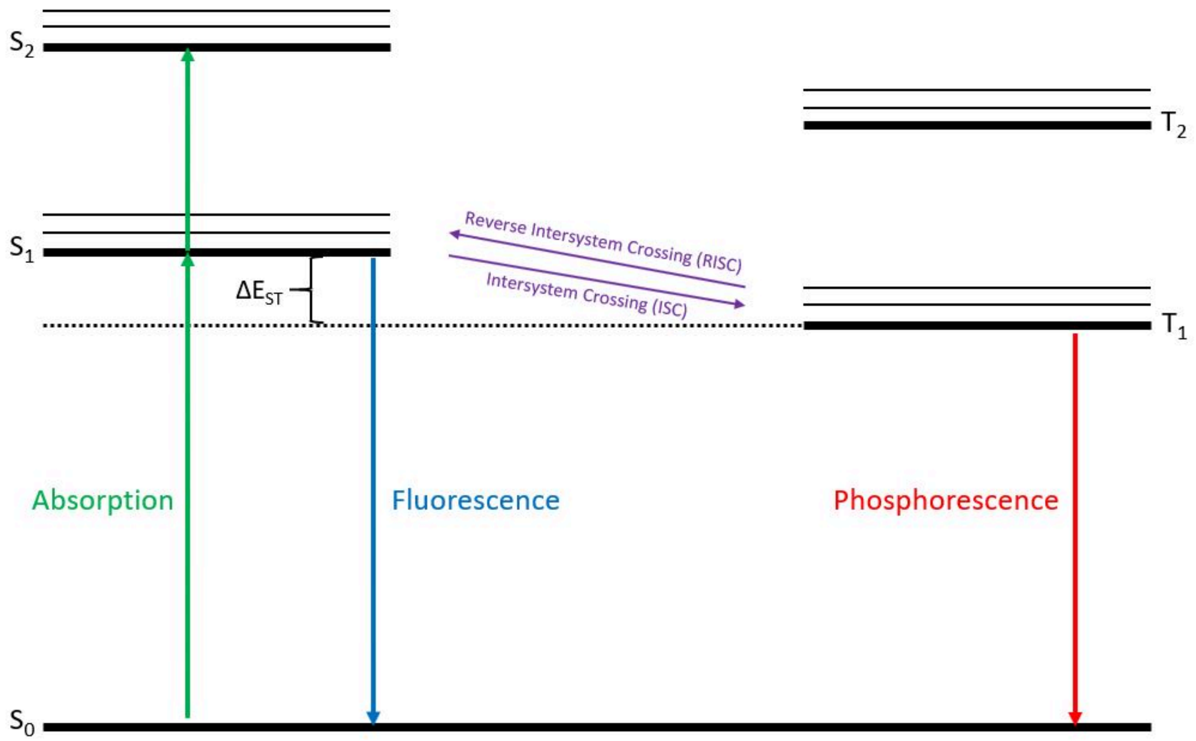
Y = A
X = B
E = C
A = D
D = E
B = F
C = G
1 = Q
2 = R
3 = S
4 = T
M = electron carrier
N = hole carrier
X = Ru+
Y = Ru3+

Reference:
Muller, S., Rudmann, H., Rubner, M., & Sevian, H. (2004). Using Organic Light-Emitting Electrochemical Thin-Film Devices To Teach Materials Science. Journal of Chemical Education, 81(11), 1620.

The first OLEDs employed **(Q)fluorescent/phosphorescent** emitters, where radiative decay occurred only from the **(M)singlet/triplet** state. Due to spin statistics, **A%** of the generated excitons are singlets and **B%** triplets. This gives a maximum possible internal quantum efficiency of **C%**. This is an **(I)allowed/forbidden** transition on the **(K)nanosecond/millisecond** time scale.

A considerable improvement came with OLEDs, which used **(R)fluorescent/phosphorescent** emitters. This mechanism exploits the heavy-atom effect where the typically used platinoid metals increase spin-orbit coupling and thus accelerate intersystem crossing (ISC) from **(N)singlet/triplet** to **(O)singlet/triplet** excited states and radiative decay to the ground state. This enables the maximum **D%** internal quantum efficiency. This is a **(J)allowed/forbidden** transition on the **(L)nanosecond/millisecond** time scale.

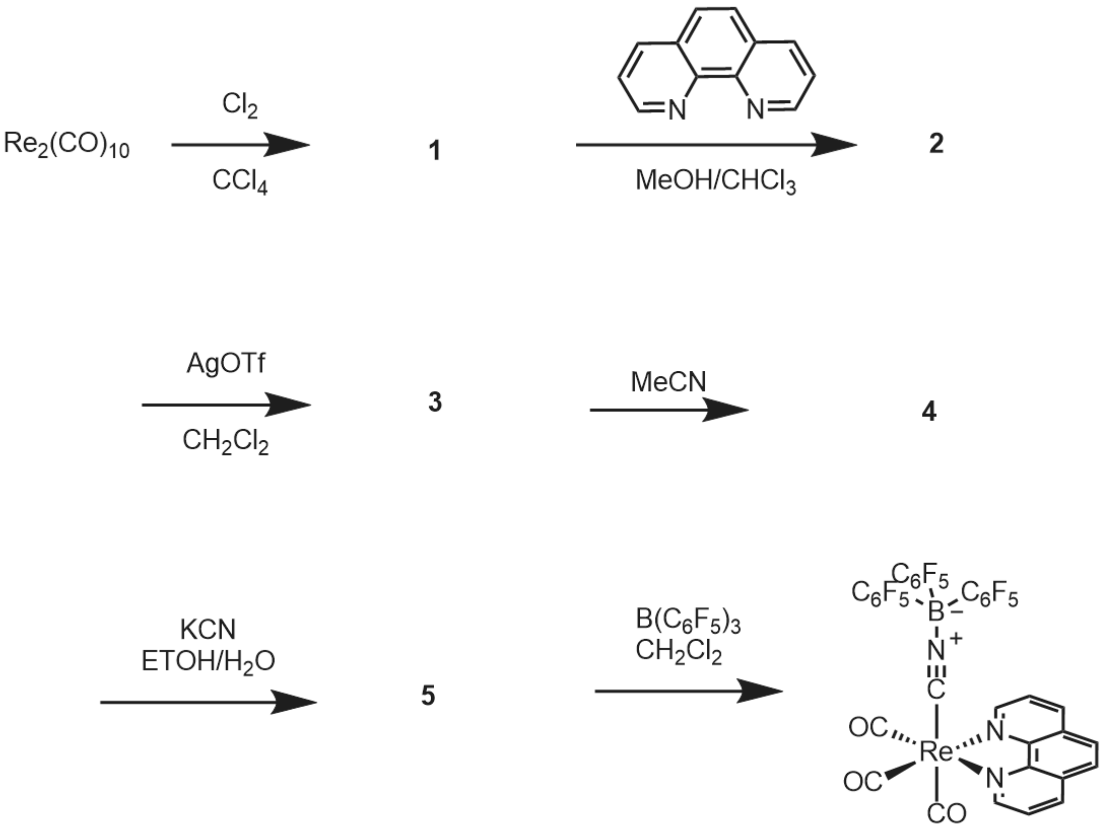
The most recent significant advance in emitter design was the introduction of TADF (thermally activated delayed fluorescence) compounds, kickstarting a new class of OLEDs. Reverse intersystem crossing (RISC) is enabled in compounds that possess a small energy gap between the S_1 and T_1 states (ΔE_{st}). Considering the timescale of fluorescence and phosphorescence transition, we see that an excited TADF material mainly emits **(S)fluorescent/phosphorescent** light. And the maximum internal quantum efficiency is **E%**.



9.2 **<u>Deduce</u>** the number **A** to **E**, process **Q**, **R,** and **S** (fluorescent or phosphorescent), the state **M**, **N**, and **O** (singlet or triplet), the transition **I** and **J** (allowed or forbidden), and the timescale **K** and **L** (nanosecond or millisecond). Provide your answer in the format A/B/C/D/E/Q/R/S/M/N/O/I/J/K/L. Be sure to look at the figure above.

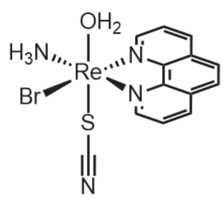
A = 25%
B = 75%
C = 25%
D = 100%
E = 100%
Q = fluorescent
R = phosphorescent
S = fluorescent
M = singlet
N = singlet
O = triplet
I= allowed
J = forbidden
K = nanosecond
L = millisecond

With this knowledge, she's ready to make the actual OLED compound. She decided first to synthesize the sky-blue phosphorescent rhenium(I) complex. Please help Sparkle complete her synthesis; the scheme is provided below.



9.3 **<u>Type</u>** the structure from 1 to 5. Use the numbering system figure (a) in the format of Re(1)(2)(3)(4)(5)(6); for example, if complex 3 is the complex in figure (b), type 3.Re(OH2)(phen)(phen)(Br)(NH3)(SCN).

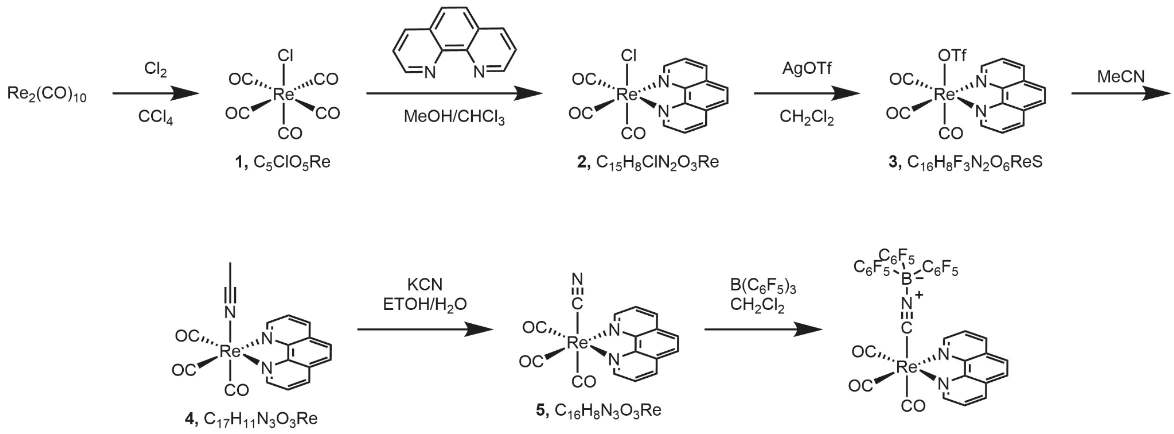
(a)



(b)

1. Re(Cl)(CO)(CO)(CO)(CO)(CO)
2. Re(Cl)(phen)(phen)(CO)(CO)(CO)

3. Re(OTf)(phen)(phen)(CO)(CO)(CO)
4. Re(NCMe)(phen)(phen)(CO)(CO)(CO)
5. Re(CN)p(hen)(phen)(CO)(CO)(CO)



references:

1. Chu, W.K., Ko, C.C., Chan, K.C., Yiu, S.M., Wong, F.L., Lee, C.S., & Roy, V. (2014). A Simple Design for Strongly Emissive Sky-Blue Phosphorescent Neutral Rhenium Complexes: Synthesis, Photophysics, and Electroluminescent Devices. Chemistry of Materials, 26(8), 2544-2550.
2. Chakraborty I, Jimenez J, Sameera WM, Kato M, Mascharak PK. Luminescent Re(I) Carbonyl Complexes as Trackable PhotoCORMs for CO delivery to Cellular Targets. Inorg Chem. 2017 Mar 6;56(5):2863-2873. doi: 10.1021/acs.inorgchem.6b02999. Epub 2017 Feb 22. PMID: 28225252; PMCID: PMC5731781.

Problem 10	Question	10.1	10.2	10.3	Bonus	Total
	Points	4	4	4	4	16

Problem 10: Complex Complexes

by Gerardo Y. Angeles (México) (naphtalenemx)

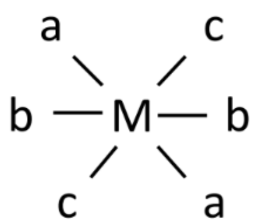
A famous chef is in a gingerbread cookie competition. To win, the chef searches for an old recipe book. The chef was happy because even though the recipe book was very old, the ingredients were clearly visible. The recipe is listed below:

Ingredients for the cookie dough:
2 eggs
3 tablespoons of butter
1 stainless steel screw
250 grams flour
2 teaspoons yeast
3 formula coordination complexes: Mabcdef, Maabcde, Maaabcd
1 kg of uranium

The chef prepared the dough but… it tasted very bad! He tried everything but nothing worked, what the recipe did not specify is which stereoisomer of the coordination compounds should be used. So the chef must try each one.

Use this format to answer:

(aa)(bb)(cc) =



10.1 **Find** all stereoisomers, not including enantiomers, of the formula Maaabcd.

M(aa)(ab)(cd), M(aa)(ac)(bd), M(aa)(ad)(bc), M(ab)(ac)(ad)

10.2 **<u>Find</u>** all stereoisomers, not including enantiomers, of the formula Maabbcd.

M(aa)(bb)(cd), M(aa)(bc)(bd), M(ab)(ab)(cd), M(ab)(ac)(bd), M(ab)(ad)(bc), M(ac)(ad)(bb)

10.3 **<u>Find</u>** all stereoisomers, not including enantiomers, of the formula Mabcdef.

M(ab)(cd)(ef), M(ab)(ce)(df), M(ab)(cf)(de), M(ac)(bd)(ef), M(ac)(be)(df), M(ac)(bf)(de), M(ad) (bc)(ef), M(ad)(be)(cf), M(ad)(bf)(ce), M(ae) (bc)(df), M(ae)(bd)(cf), M(ae)(bf)(cd) M(af) (bc)(de), M(af) (bd)(ce), M(af)(be)(cd)

Problem 11	Question	11.1	11.2	11.3	Bonus	Total
	Points	4	4	4	4	16

Problem 11: 原來你也玩崩壞星穹鐵道 (gold, physical)

by Pin-Jui Lin (nightlight_1201), Taiwan

Sparkle is a five-star, harmony, quantum character in Honkai Star Rail. So, let's end with a quantum problem. A particle is in a one-dimensional box with infinite walls at $x = \pm 0.5a$ where $a > 0$. At $t = 0$, the particle obeys the following wave function,

$$\Psi(x, t = 0) = \begin{cases} \gamma & -\frac{a}{2} < x < 0 \\ -\gamma & 0 < x < \frac{a}{2} \\ 0 & \text{elsewhere} \end{cases}$$

11.1 **Find** the value of γ.

$$\gamma^2 \cdot a = 1 \implies \boxed{\gamma = \sqrt{\frac{1}{a}}}$$

11.2 **<u>Find</u>** eigenfunction and energy eigenvalue using the time-dependent Schrödinger equation.

$$\Psi_n(x,t) = \psi_n(x) \cdot e^{-iE_n t/\hbar}$$

$$\psi_n(x,t) = \begin{cases} \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) & n = 2,4,6\ldots \\ \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi x}{a}\right) & n = 1,3,5\ldots \end{cases}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma} \qquad , n = 1,2,3\ldots$$

Any sensible equation representation is accepted, such as Re(e^iφx) and Im(e^iφx).

11.3 **Calculate** the probability of measuring the energy of the first excited state at $t = 0$.

$$\Psi(x, t=0) = \sum_n c_n \psi_n(x)$$

$$\int_{-\infty}^{\infty} \psi_m^*(x)\Psi(x,t=0)\,dx = \sum_n c_n \int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\,dx = \sum_n c_n \delta_{nm} = c_m$$

$$\begin{aligned}
c_2 &= \int_{-\frac{a}{2}}^{0} \psi_2(x)\Psi(x,t=0)\,dx + \int_0^{\frac{a}{2}} \psi_2(x)\Psi(x,t=0)\,dx \\
&= \int_{-\frac{a}{2}}^{0} \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)\cdot\sqrt{\frac{1}{a}}\,dx + \int_0^{\frac{a}{2}} \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)\cdot -\sqrt{\frac{1}{a}}\,dx \\
&= \frac{\sqrt{2}}{a}\left(-\cos\left(\frac{2\pi x}{a}\right)\cdot\frac{a}{2\pi}\right)\Bigg|_{x=-\frac{a}{2}}^{x=0} - \frac{\sqrt{2}}{a}\left(-\cos\left(\frac{2\pi x}{a}\right)\cdot\frac{a}{2\pi}\right)\Bigg|_{x=0}^{x=\frac{a}{2}} \\
&= \frac{\sqrt{2}}{2\pi}(-1-1) - \frac{\sqrt{2}}{2\pi}(1+1) \\
&= -\frac{2\sqrt{2}}{\pi}
\end{aligned}$$

$$\implies \boxed{|c_2|^2 = \frac{8}{\pi^2}}$$

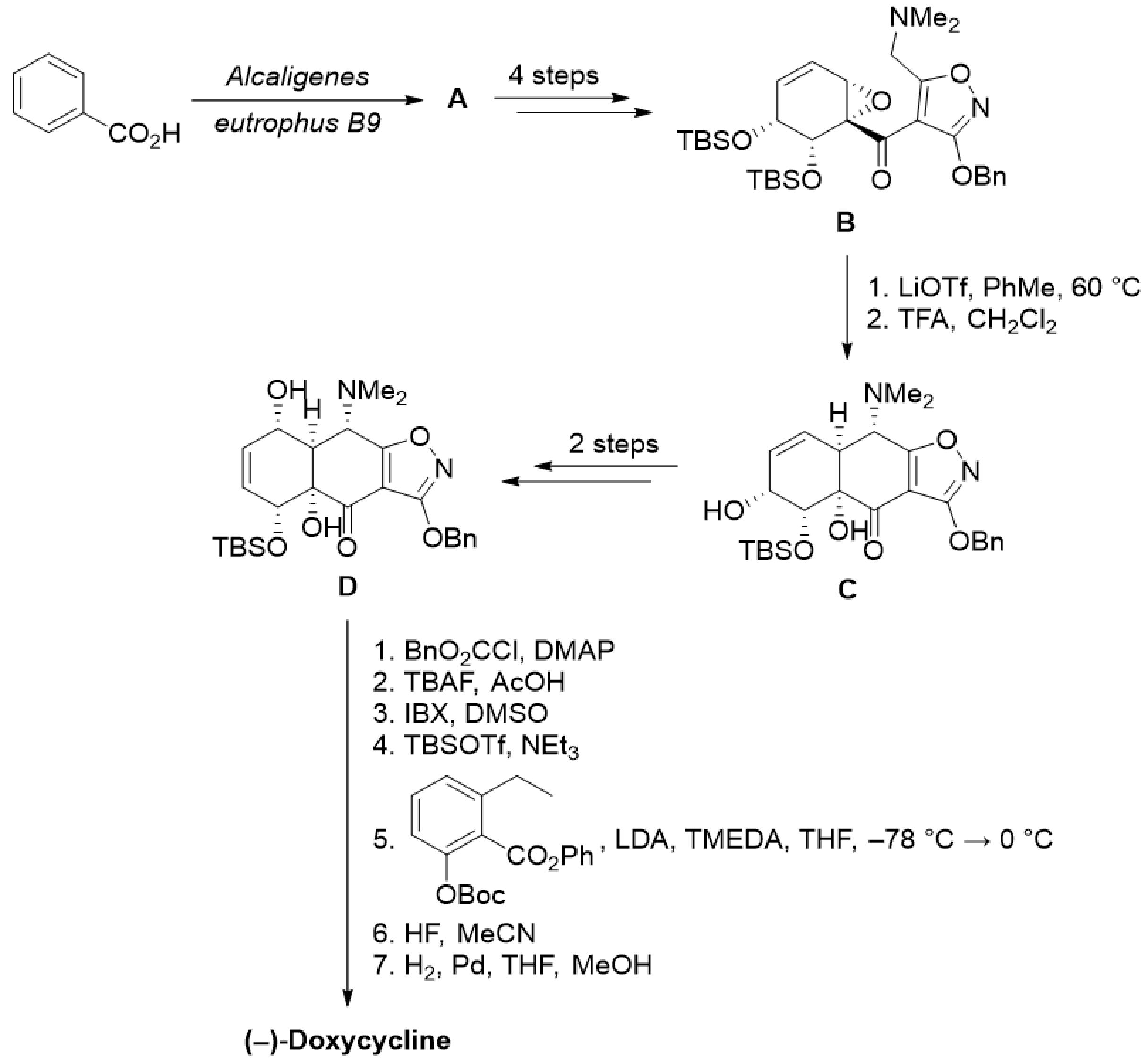
Or 81.06%.

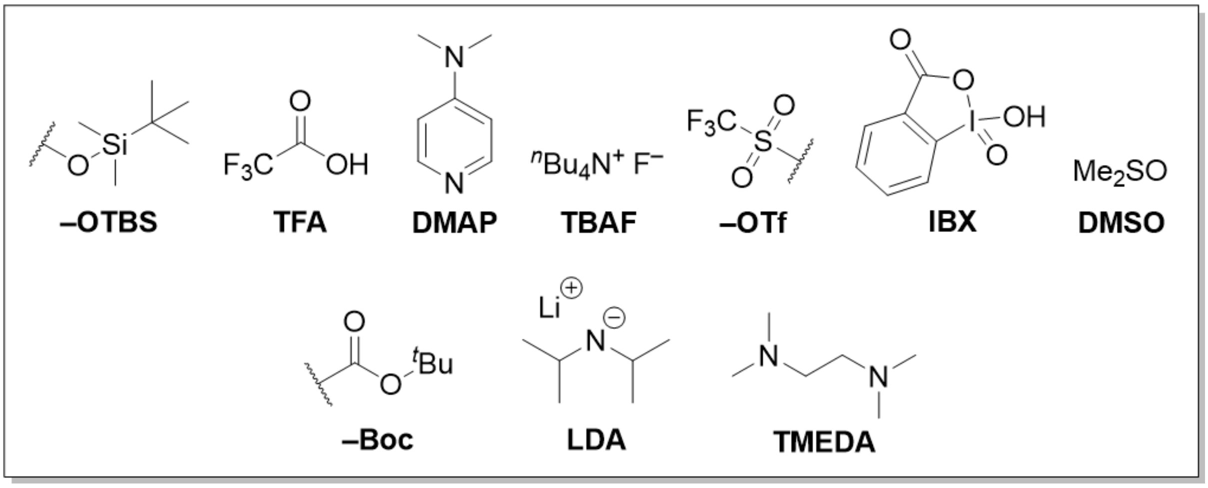
Problem 12	Question	12.1	12.2	12.3	Bonus	Total
	Points	4	4	4	4	16

Problem 12: Doxycycline

by Ranen Yong, Singapore

Doxycycline is an antibiotic that is commonly used to treat bacterial pneumonia, acne, chlamydia infections, Lyme disease, cholera, typhus, and syphilis. A synthesis method for doxycycline is shown below.





In the first step, a mutant strain of *Alcaligenes eutrophus* was used to synthesize compound **A**. The ^{1}H NMR spectrum of compound **A** is given below:

δ_H(400 MHz, $CDCl_3$) / ppm: 10 (broad s, 1H), 6.2 (dd, 1H, J = 9.5, 5.0 Hz), 6.0 (m, 1H), 5.9 (m, 1H), 4.9 (broad d, 1H, J = 10 Hz), 3.6 (s, 1H), 2.6 (d, 1H, J = 10 Hz)

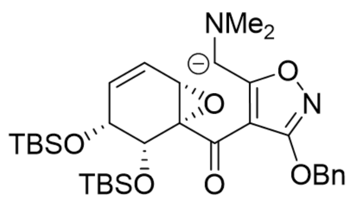
12.1 **State** all functional group(s) present in compound **A**. **How** many times does each of the functional group(s) appear in compound **A**? All functional groups and their frequencies must be correct for credit to be awarded.

Alcohol – 2
Carboxylic acid – 1
Alkene – 2

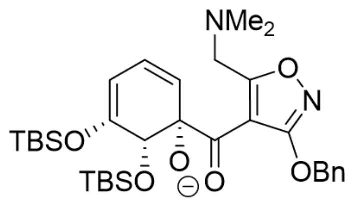
In the transformation of compound **B** to compound **C**, it is known that the intermediate(s) is/are formed before the addition of TFA in CH_2Cl_2.

12.2 **Select** all intermediate(s) formed during this transformation.

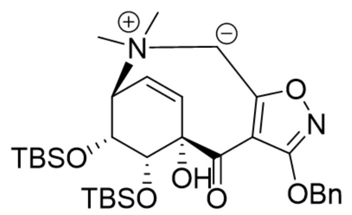
C and **D**



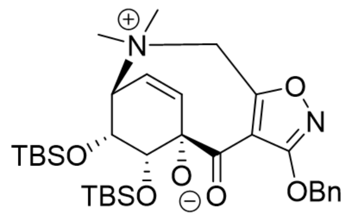
A



B

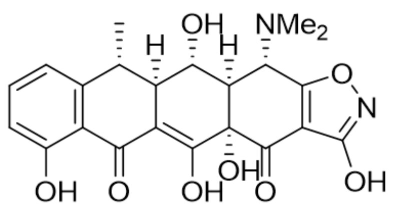


C

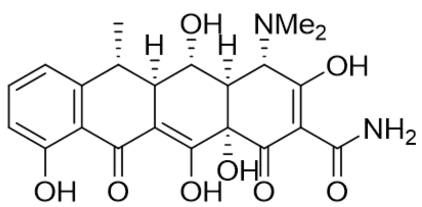


D

12.3 Of the following options below, **<u>which</u>** is the correct structure of (–)-doxycycline?



A



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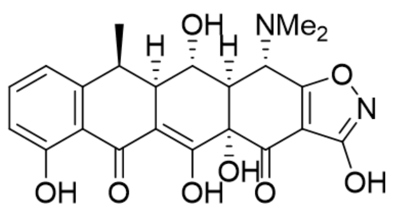

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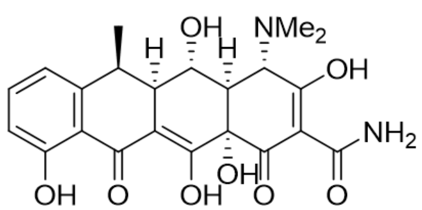

D

B