

International
Meme Chemistry
Olympiad
2021
Spring

Official English problems

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Introduction

Rules

- You **may** use any available resources to solve the tasks, including the internet, books and calculators of any kind.
- You **may not** communicate with anyone outside of your team during the olympiad.
- You **must** submit the paper on time through Google Classroom or by sending it to memechemistryolympiad@gmail.com. Otherwise, the submission will close and your work will not be reviewed.
- Write your solutions in the **respective boxes** below each task. If using paper to complete the tasks, paste scans of the papers into the boxes. Your submission must be final - you may **not** link to your work, only attach the work itself.
- Miscalculations **will not** be awarded full marks.
- There is **no** penalty for wrong answers.
- **Show your work** in the submissions. Otherwise, the work **will not** be awarded full marks.
- Beware that **you** are responsible for the quality of your work. Corrupted files or otherwise unreadable submissions **will not be graded** if none of the organisers can open it.
- You **must** laugh at all the jokes.
- In case of technical problems write to memechemistryolympiad@gmail.com

A few words by the authors

We would like to thank the following people for participating in helping the development of our Olympiad or for their financial aid:

John Leung
Džonatans Miks Melgalvis
Aleksandr Evsyukov
Aleksandrs Morozovs

and other people who decided to stay anonymous, as well as the Young Folks LV organization and the "Himik-Psihopat" VK community.

We wish you a lot of fun while solving the Olympiad.

See you in June 2021 at the next Meme Chemistry Olympiad!

Physical and Chemical formulas and constants

electric current	$I = \frac{Q}{t}$
moles	$n = \frac{m}{M}$
ideal gas law	$pV = nRT$
volume of a gas at given conditions	$V = n * V_0$
charge	$Q = F * n$
photon energy	$E = h\nu$
molar concentration	$c = \frac{n}{V}$
mass concentration	$\omega_A = \frac{m_A}{m_{mixture}}$
molar fraction	$X_A = \frac{n_A}{n_{mixture}}$
mass from density	$m = \rho V$
pH	$pH = -\log_{10}[H^+]$
amount of molecules	$N = nNa$
molar volume at given conditions	$V_0 = \frac{RT}{p} * 1000L$

universal gas constant	$R = 8.314 J/(mol * K)$
electron charge	$q = 1.6 * 10^{-19} C$
Faraday constant	$F = 96485 C/mol$
Avogadro constant	$Na = 6.021 * 10^{23} mol^{-1}$
Planck constant	$h = 6.63 * 10^{-34} J * s$
molar volume of a gas at STP	$V_0 = 22.4L/mol$
water dissociation constant at 298 K	$K_w = 10^{-14}$

Periodic Table

Periodic Table of the Elements

1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.887	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.227	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine 209	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Nh Nihonium unknown	114 Fl Flerovium [289]	115 Mc Moscovium unknown	116 Lv Livermorium [293]	117 Ts Tennessine unknown	118 Og Oganesson unknown
57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium [144.913]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967			
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]			

Alkali Metal

Alkaline Earth

Transition Metal

Basic Metal

Semimetal

Nonmetal

Halogen

Noble Gas

Lanthanide

Actinide

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You can find a periodic table in a higher resolution at <https://periodictable.com>

Solubility chart for ionic compounds

Solubility Chart

	acetate	bromide	carbonate	chlorate	chloride	chromate	hydroxide	iodide	nitrate	oxide	phosphate	silicate	sulfate	sulfide
aluminum	S	S	-	S	S	-	A	S	S	a	A	I	S	d
ammonium	S	S	S	S	S	S	-	S	S	-	S	-	S	S
barium	S	S	P	S	S	A	S	S	S	S	A	S	a	d
calcium	S	S	P	S	S	S	P	S	S	P	P	P	P	P
copper(II)	S	S	-	S	S	-	A	-	S	A	A	A	S	A
hydrogen	S	S	-	S	S	-	-	S	S	-	S	I	S	S
iron(II)	S	S	P	S	S	-	A	S	S	A	A	-	S	A
iron(III)	S	S	-	S	S	A	A	S	S	A	P	-	P	d
lead(II)	S	S	A	S	S	A	P	P	S	P	A	A	P	A
magnesium	S	S	P	S	S	S	A	S	S	A	P	A	S	d
manganese(II)	S	S	P	S	S	-	A	S	S	A	P	I	S	A
mercury(I)	P	A	A	S	a	P	-	A	S	A	A	-	P	I
mercury(II)	S	S	-	S	S	P	A	P	S	P	A	-	d	I
potassium	S	S	S	S	S	S	S	S	S	S	S	S	S	S
silver	P	a	A	S	a	P	-	I	S	P	A	-	P	A
sodium	S	S	S	S	S	S	S	S	S	S	S	S	S	S
strontium	S	S	P	S	S	P	S	S	S	S	A	A	P	S
tin(II)	d	S	-	S	S	A	A	S	d	A	A	-	S	A
tin(IV)	S	S	-	-	S	S	P	d	-	A	-	-	S	A
zinc	S	S	P	S	S	P	A	S	S	P	A	A	S	A

S=soluble in water. P=partially soluble in water, soluble in dilute acids. A=soluble in acids, insoluble in water. a=slightly soluble in acids, insoluble in water. I=insoluble in dilute acids and in water. d=decomposes in water

Olympiad tasks

Part 1- General Chemistry

Problem 1. Mixing chemicals is fun!

High school student Tom persuaded his rich parents to buy him a chemistry lab because he liked chemistry (at least, high-school level inorganic). Unfortunately, the lab his parents bought him as a birthday gift was quite old and didn't have so many glassware and reagents. Little Tom had only a few reagents which he decided to mix together. But, he also found three reagents in unlabelled jars. We will refer to them as reagents **A**, **B** and **C** correspondingly. Compound **A** is a black powder which reacts with hydrochloric acid as well as produces a vigorous reaction when combined with hydrogen peroxide. If compound **A** is heated in a flow of hydrogen, a metallic solid is formed which can react with hydrochloric acid and produce a pink solution, which after evaporating gives a pink precipitate. Compound **A** can also be reacted with molten potassium nitrate in presence of potassium hydroxide, forming a dark solid that is green in water solution and also quickly disproportionates, forming compound **A** and a purple solution with antibacterial properties. Compound **B** is also a water insoluble black solid. Compound **B** can be dissolved by adding excessive **B** to 0.1M KOH solution, forming a brown-dark orange coloured solution which also has antibacterial properties. One of the reaction products can be added to table salt as a mineral supplement. The solution produced, when acidified by dilute sulfuric acid, produces compound **B** again as well as potassium sulfate and water. Compound **B** can be melted and boiled at low temperatures, **B** vapors are very toxic. Also, compound **B**, when added in excess to methyl ethyl ketone and then treated with aqueous base produces a yellow precipitate. Compound **B** also reacts with compound **C**. Compound **C** forms beautiful crystals. It is produced by boiling aqueous sodium hydroxide with excessive sulfur. It has strong reductive properties and is used in analytical chemistry and as a cleaning agent to dispose of oxidisers in laboratories. It is also used in medicine as an antidote for cyanide poisoning. Hint: compound **C** contains oxygen.

Write the molecular formulas of compounds **A**, **B** and **C** in the table below. 9p

compound A	compound B	compound C

Write balanced molecular reaction equations which describe all the processes mentioned in the text above (*11 equations in total*) on a separate sheet of paper and attach an image/scan copy of it when submitting the olympiad tasks.

Problem 2. Anastasia and the copper shower

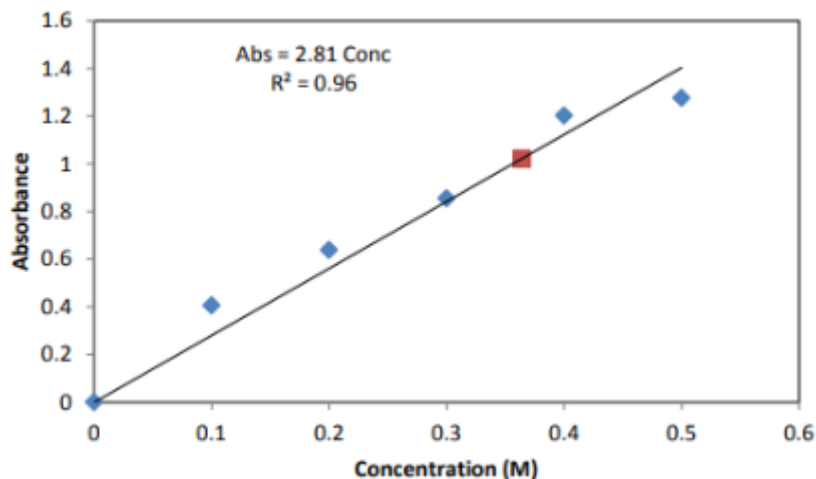
Once upon a time, Anastasia endured a copper sulfate shower. Her lab coat turned blue. Nastya wants to know the concentration of the compound in her lab coat. To find the concentration, we take a sample of a different solution with the sulfate and derive an equation that can find the concentration.

The dependence of absorption on concentration can be approximated as such:

$$A = \epsilon cl$$

Where A - absorbance, ϵ - molar absorptivity, c - concentration, l - length of the cuvette (a little container with the sample with which measurements are made).

Absorbance was plotted against concentration in the following graph.



The trendline equation is:

$$A = 2.81c$$

Determine the molar absorptivity (ϵ) if length of the cuvette (l) equals 3 cm.

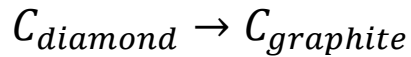
Assume Nastya's lab coat is a cuvette with a length of 1 millimeter. The absorbance reading of her lab coat is 0.04.

Determine the concentration of copper sulfate in her lab coat.

Problem 3. Impossible or reversible?

At one point, Nick heard someone say that “a reaction is reversible if it’s impossible”. While of course this isn’t true, let’s look at a case where a reaction is impossible but reversible.

The conversion of diamond to graphite is thermodynamically favorable and reversible, but very, very slow. The reaction equation is as follows:



In this task, you will determine the equilibrium constant (K) and half life ($t_{1/2}$) of this reaction.

The Gibbs free energy of this reaction is -2.90 kJ/mol.

Determine, using the formula $\Delta G = -RT \ln K$, the equilibrium constant for this reaction at 273 K.

The rate constant for the forward reaction is $6.93 \times 10^{-81} \text{ s}^{-1}$.

Determine the half life of diamond conversion to graphite using the formula $t = \ln(0.5)/-k$

Write the reaction equation for the reverse reaction.

Determine the reverse reaction rate constant (remember that $K = \frac{k_{forward}}{k_{reverse}}$).

Problem 4. Agatha and a white powder

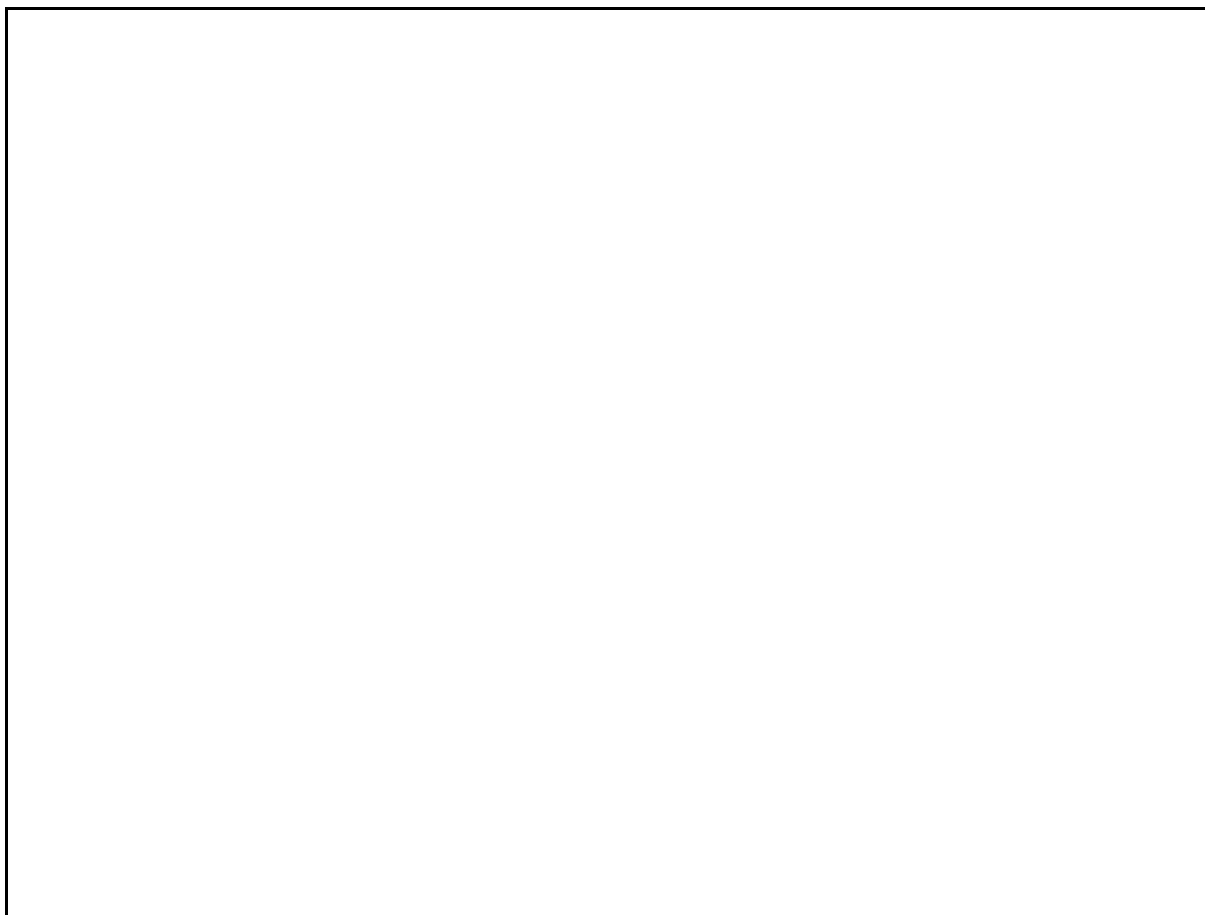
Recently, organic chemist Agatha discovered an unknown white powder in her lab cabinet. As a true organic chemist, the first test she carried out to find out the substance formula is an ^1H NMR spectroscopic analysis. This test is used to find out the frequencies at which the ^1H nuclei (protons) resonate in a molecule when it is subjected to a very strong magnetic field, giving the user information about the molecule's H atom count, the way they are coupled and some functional groups. Strangely, this test produced an absolutely empty spectrum (no H resonance was observed). Because the NMR machine could also do a ^{13}C NMR spectrum (this method is absolutely the same as ^1H NMR but gives information about C atoms), Agatha made that analysis too. The ^{13}C NMR also produced an empty spectrum, leaving Agatha in shock. She was worried that the NMR machine didn't work properly, so she carried out an NMR analysis of an already known compound TMS (tetramethylsilane) and everything was fine, so the machine was alright. She also wanted to carry out a mass spectroscopy analysis on the sample, but the only mass spectrometer the research institute where Agatha was working had was on maintenance, thus forcing her to use old-school analytical methods to determine what that mysterious white powder was.

Which information can Agatha extract from the seemingly useless NMR analysis? Explain your thoughts.



The test Agatha conducted was as follows: First of all, she tried to dissolve the white powder in water, the powder was quite soluble and formed a clear uncoloured solution. Then Agatha slowly added a part of the solution to a beaker of aqueous barium nitrate and observed precipitation of a white compound. Agatha filtered the precipitate and started experimenting with it. The precipitate dissolved in hydrochloric acid, releasing a gas. Then Agatha heated 2.050g the precipitate in a crucible at 1300K temperature for a few hours. The leftover solid with a mass of 1.440g reacted with water and produced a basic solution. Then Agatha mixed the rest of the solution with a solution of a lead(II) salt, a white precipitate appeared again. Agatha also tried heating the white powder itself, at the end of the process Agatha's 2.450g of the white powder decreased in mass by 1.240g.

What is the white powder's chemical formula? Explain your thoughts.



Write the ionic half-reaction equations describing the reactions during the tests Agatha had performed when she mixed the white powder with different chemicals in solution as well as balanced molecular reaction equations of the heating processes. (6 equations in total)



Problem 5. Little Ian vs a bathtub

Little Ian decided to use his iron bathtub to store sulfuric acid. But, his friend Tom told him that concentrated sulfuric acid would immediately dissolve the bathtub, leaving Ian with no place to wash himself in. Little Ian definitely listened to Tom's advice and poured in 100 liters of concentrated 98% sulfuric acid in the bathtub. Tom was observing the whole spectacle hoping that little Ian would die in the process. Unfortunately little Ian and the bathtub survived the experiment.

Explain why didn't the bathtub get destroyed during the experiment.

Little Ian found out that on reaction of copper metal and concentrated sulfuric acid a very stinky gas is produced so he decided to prank Tom who was sharing the apartment with Ian by spreading the incredibly pleasant smell throughout the apartment. So, little Ian bought a few kilograms of copper tubing and threw it all into the bathtub. The really stinky gas got produced but unfortunately during the process which is extremely exothermic all 100L of sulfuric acid boiled away, leaving behind two solids **A** and **B**. These solids are produced either by the reaction of copper and sulfuric acid or as a product of the dissolution of the bathtub during the exact same reaction and contain no water. Solid **B** is white, solid **A** is brown.

Provide 2 reasons for why the bathtub started dissolving in sulfuric acid after the addition of copper metal.

Which chemical compounds are **A** and **B**? **Write** their names below.

A

B

Calculate the amount of the gas (in moles) produced by the reaction in total if there were 4000g of A and 8000g of B produced.

The conditions in little Ian's bathroom are as follows: pressure is equal to 1300 mm Hg, temperature to 207 C.

Determine the volume occupied by the gas assuming it is an ideal gas.

For the next experiment Ian bought a ceramic bathtub to avoid such mishaps in the future. In the bathtub he poured in 5L of concentrated 98% sulfuric acid, Tom wasn't interested in that thing anymore. Ian googled that throwing in a bunch of sodium will result in a production of an even stinkier gas. Unfortunately little Ian didn't have pure sodium, he only had an alloy of sodium and potassium (NaK) in a 2L jar. So, little Ian poured¹ in the contents of the NaK jar into the bathtub and witnessed an explosion.

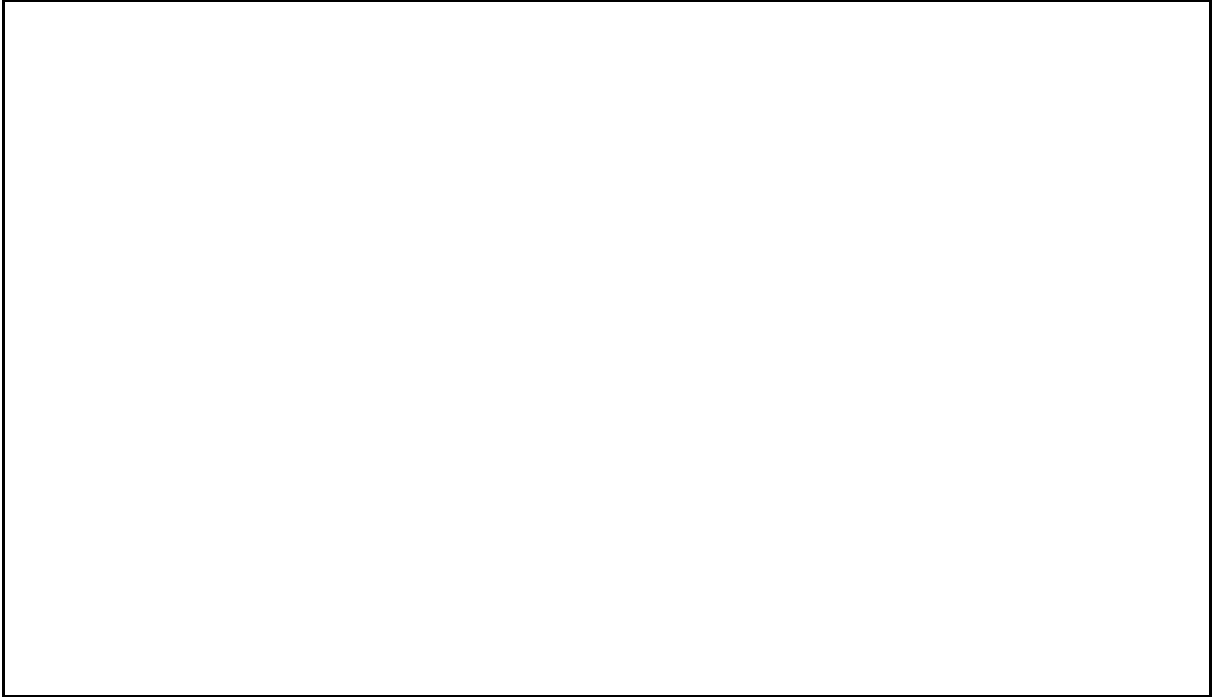
Little Ian recalled the situation where he was throwing pieces of sodium into a river in order to make the river boil and he thought the explosion happened because of similar reasons why the river boiled.

Which reasons did little Ian mean? **Write** it down (*at least two*)

Because little Ian had to dispose of the rest of NaK somehow, he went outside and poured it into a pond. He poured in 10kg of NaK, and he witnessed that 3332L (at STP) of gas was produced on its reaction with water. Assume that the gas contains no water vapour and that all of the NaK reacted with water.

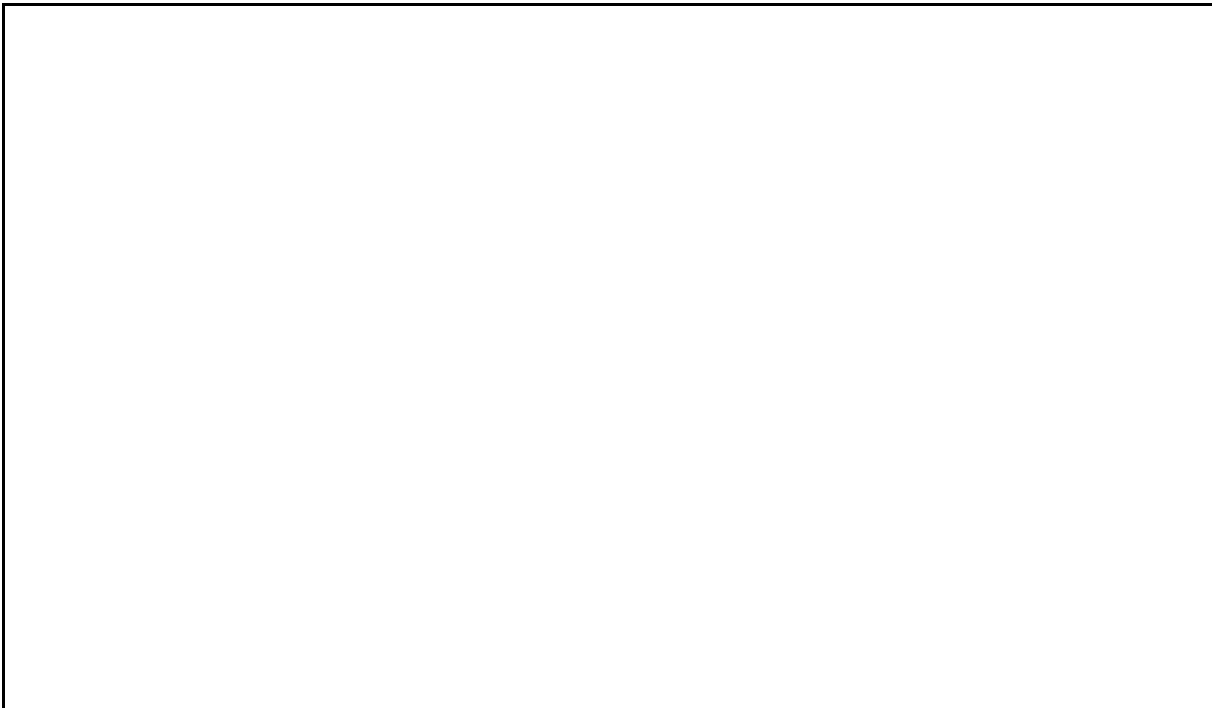
¹ Sodium-potassium alloy is a liquid at room temperature

Determine the mass concentration of sodium and potassium in the alloy.



Consider the pond being a 595 m^3 vessel of water. You can neglect the mass of water spent in the reaction as well as the change in density of the water after the reaction.

Calculate the pH of the pond after little Ian disposed of his NaK alloy in the pond.



Problem 6. Aqua regia and its positive effects on health

Jonathan has recently participated in the Chemistry Olympiad and just got his gold medal. But, sadly, one vengeant girl he had rejected dating had stolen Jonathan's gold medal while he was asleep. Jonathan has already suspected that that girl might have stolen his medal so he visited her. The vengeant girl had crushed Jonathan's medal with a hammer and gave it back to him. Jonathan decided to separate all the gold and all the other valuable metals from the medal and to re-cast it afterwards. He made an elemental analysis and found out the medal is an alloy of iron, copper, gold and silver. He devised the following procedure to separate the valuable metals:

The Chemistry Olympiad gold medal with a mass of 60.00g was first treated with hydrochloric acid, 8.00L (at STP) of gas were collected during the reaction. When bubbling stopped the medal was treated with aqua regia and got fully dissolved after a minute. The dissolved medal was afterwards mixed with an excessive amount of conc. NaCl solution. A white precipitate appeared. The precipitate was filtered out, and the remaining solution was treated with a solution of iron (II) sulfate, producing a brown precipitate of gold. The precipitate was filtered, dried and then mixed with boiling nitric acid. After 5 minutes of stirring the precipitate was transferred to a vacuum filter filtered off. Jonathan then washed the precipitate with a saturated sodium hydroxide solution and water a few times. He left the vacuum pump on for 5 minutes to dry the precipitate as much as possible and then he weighed it. The pure gold he extracted from the medal weighed 1.80 g. He also took the white precipitate he had acquired already, and dissolved it in conc. HNO_3 . Afterwards Jonathan put the solution into a large beaker and diluted it to a volume of 1L. He inserted two platinum electrodes in the beaker and connected the power source. He electrolyzed the solution with a current $I = 5A$ and a voltage $U = 12V$ until the cathode didn't start actively producing a gas. The electrolysis process took 4438 seconds of time to be completed.

Which metal was extracted using electrolysis? **Write** the chemical element symbol.

Write the electrolysis cathode and anode half-reaction equations as well as the net reaction equation. (3 equations in total)

Write the balanced molecular reaction equation describing gold dissolving in aqua regia. (Hint: gold is a Lewis acid which can form complexes with 4 ligands)

Write the balanced half-reaction equation for the reaction between iron sulfate and dissolved gold (Hint: it is a redox reaction)

Calculate the mass of the metal produced by electrolysis. Use Faraday's constant $F = 96485 \text{ C/mol}$, assume that during the electrolysis only the metal was reduced.

Calculate the composition (the concentration in mass % of each metal) of the medal. Provide your calculations, assume that all extractions have 100% yield.

Problem 7. Halogens and their derivatives

Chemistry student Nick found a strange chemistry-themed blog on the Internet. Nick really doubted some of the contents were true so he decided to carry out some research to find out if the information on the blog is true.

Below will be listed 20 phrases from that blog, you will have to **decide** whether they are true or false.

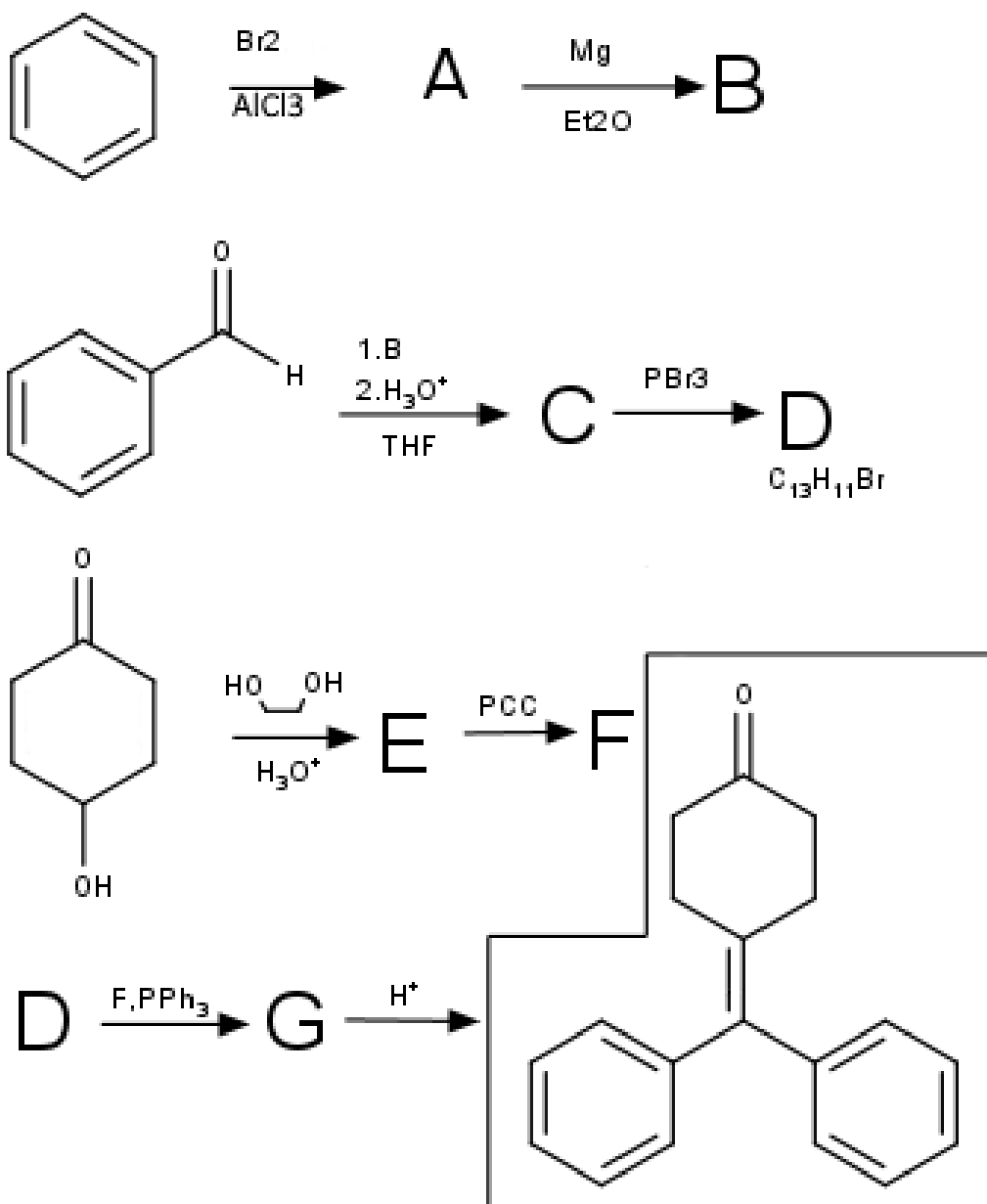
0. *T Chlorine is one of the halogens.*
1. Potassium perchlorate is also called Bertolle's salt.
2. When potassium iodide is mixed with bromine, a dark brown precipitate of iodine forms.
3. Iodine never melts at atmospheric pressure, it sublimates.
4. A compound with the formula ClF_5 can not exist.
5. Sodium hypochlorite is a very strong disinfectant.
6. Bleach consists of sodium, chlorine and oxygen atoms.
7. Bromine is the only element that is liquid at 273K.
8. When water and chlorine gas react together, water oxidises the chlorine atoms to chloride ions.
9. When liquid potassium chloride is electrolyzed, on the cathode chlorine gas is formed.
10. Iodine reacts with acetone in basic conditions and produces a yellow precipitate.
11. Potassium iodide in solution reacts with iodine to form a complex.
12. The molecule with the formula CCl_4 is called chloroform.
13. When sodium hypochlorite reacts with hydrogen chloride, hypochlorite ions oxidise the chloride ions.
14. Hydrogen chloride can be oxidised by iodine to form chlorine and hydrogen iodide.
15. Chloride is a good bidentate ligand.
16. When methane is mixed with chlorine gas and treated with UV light, ethane may form.
17. Sodium chlorate is used as table salt.
18. The hypobromous acid is unstable and quickly disproportionates into perbromic acid and hydrogen bromide at room temperature.
19. If you mix 50g of NaOCl with 40g of HCl 10 L (at STP) of gas is produced.
20. When fluorine gets mixed with water, the fluorine atoms get reduced.

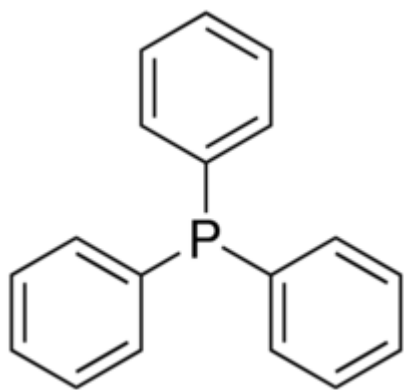
Write T or F before the phase number, T for correct statements, F for wrong ones. An example of how to report the answer is shown in the statement listed as the zeroth statement.

Part 2- Organic Chemistry

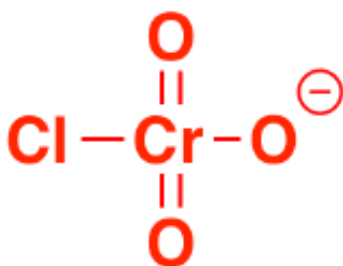
Problem 1. Synthesizing dreams

Ever since Agatha started working in an Organic Chemistry lab she wanted to synthesise one molecule. She devised the following synthesis method. Some of the intermediates and reagents are missing.

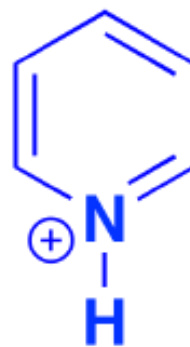




PPh₃



PCC



Fill in the structural formulas for the missing compounds **A-G** in the synthesis scheme.

A	B
C	D

E	F
G	Place for corrections (compound _)

What is the trivial name for compounds like **B**, produced in a reaction of a halocarbon with magnesium?

- a) Wittig ylid b) Grignard reagent c) Jones' reagent d) Tollens' reagent

Why is ethylene glycol added to the carbonyl compound in the synthesis of **E**? Which type of functional group does it produce?

Is the final product aromatic?

- a) yes b) no c) can't determine d) depends on the stereoisomer

Which mechanism does the **benzene=>A** step follow?

- a) ionic b) radical c) nucleophilic aromatic substitution d) electrophilic aromatic substitution

Why is Lewis acid needed in the **benzene=>A** step?

- a) as a catalyst b) to break the C-H bond in benzene c) to introduce only one bromine

Draw the mechanism for the **benzaldehyde=>C** step of the synthesis.

Will the product react with methylamine CH_3NH_2 ? If yes, provide the product structural formula.

Draw the formula of the product here, if needed. If no reaction happens write "no reaction" in this box

What will happen if we add NaNH_2 to **A**? Write the trivial name of the product.

Which reaction mechanism does the **A**+ NaNH_2 reaction follow?

a) $\text{S}_{\text{N}}1$ b) $\text{S}_{\text{N}}2$ c)benzyne mechanism d) $\text{S}_{\text{N}}\text{Ar}$

Which reaction type is **E**=>**F**?

a)reduction b)substitution c)oxidation d)addition

Name the functional group that changed in the **E**=>**F** reaction and the functional group that was produced by that reaction. Write down your answer in the table below.

Functional group in compound E	Functional group in compound F

Which reagents can be used to do the **E=>F** reaction instead of PCC?

- a) $K_2Cr_2O_7/conc\ H_2SO_4$ (Jones' reagent)
- b) m-CPBA (meta-chloroperoxybenzoic acid)
- c) SO_2
- d) oxalyl chloride+DMSO+triethylamine
- e) conc H_2SO_4

Is Agatha's synthesised molecule planar?

Which reaction is being used by Agatha in the **D=>G** step of the synthesis?

- a) Wittig reaction
- b) Mitsunobu reaction
- c) Prilezhaev reaction
- d) Appel reaction

What is the name of compound **C**?

Problem 2. You'd better not trust the IT department

Jonathan, an intern at an organic synthesis laboratory, was tasked with synthesising 10 different organic compounds by his old professor Mr. Adams. The professor sent Jonathan a synthesis scheme for each of the 10 compounds, but unfortunately the synthesis scheme file got corrupted, and Jonathan could only extract the following data from it: the precursor of the compound, the number of intermediates in the synthesis, and the product structural formula. Jonathan wanted to ask his professor to give him the original scheme the next day in the lab, but sadly Mr. Adams had been killed in a car accident on the way to the lab the next day, thus leaving Jonathan with no other choice but to logically find out which reagents will be needed for the syntheses and which intermediates are going to be produced.

Jonathan knew that all the missing reagents required for the syntheses were already ordered by Mr. Adams and arrived at the lab recently. The reagents available in Jonathan's lab are in the **Reagent Bank**. Jonathan also knew that because of the high price some of the reagents were being synthesised in situ, so some of the needed reagents in the synthesis may not be available at the lab as is and they must be made using other available reagents. The corrupted synthesis schemes as well as the list of the reagents available in the lab are located below, for simplicity's sake the missing intermediates for each reaction are marked with letters **A-D**.

Beware! A-D intermediates differ for each synthesis, they are NOT the same molecules in all 10 syntheses!!

Take note that one synthesis step may involve either adding one reagent or the reagent addition followed by the workup, or adding more than one reagent in succession order with or without the workup. Protonated or deprotonated forms of a molecule do **not** count as intermediates.

Write down the complete scheme of the syntheses **on a separate sheet of paper** by writing all the intermediate molecule structural formulas (ignore stereochemistry) as well as the reagents needed to do the reaction step (if the reagent needed is not available at the **Reagent Bank**, write the synthesis scheme for the reagent using only the chemicals available at the **Reagent Bank**) and the necessary solvents for solvent-specific reactions like Grignard reactions.

Use commonly used abbreviations (e.g Et, Me, i-Pr, Ph) as well as acronyms for the reagent names given in the Reagent Bank (PCC instead of pyridinium chlorochromate or EtOH instead of C₂H₅OH)

Please attach the scheme as an image or a scan to the olympiad tasks when submitting, otherwise the task will not be graded.

Draw the mechanisms of the first 2 steps involved in the synthesis No.5 on another sheet of paper and also attach it to your olympiad tasks when submitting the olympiad solutions.

Which reaction is the last step in the 10th synthesis? Write down the reaction name under the reaction arrow on your scheme.

Circle all the synthesis scheme numbers that require usage of a Grignard reagent on your scheme.

Which of the reaction steps in the syntheses will most probably be a Mitsunobu reaction?

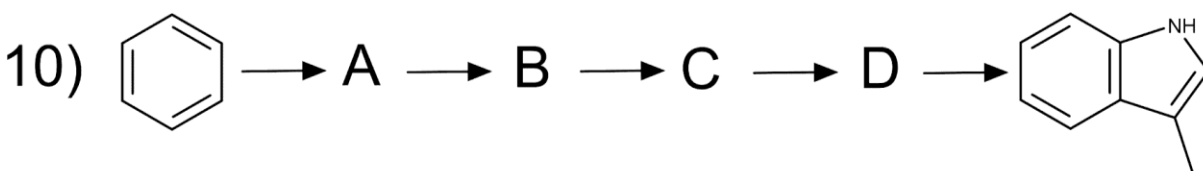
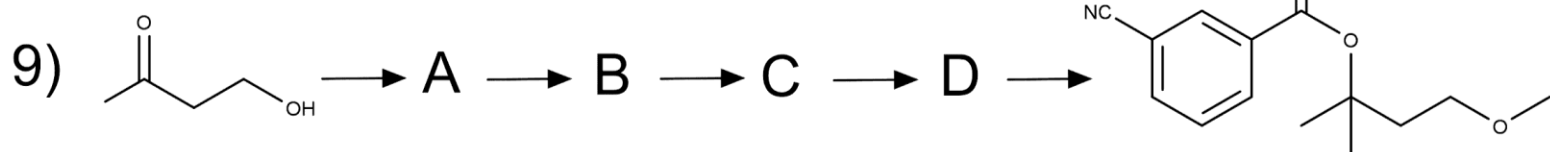
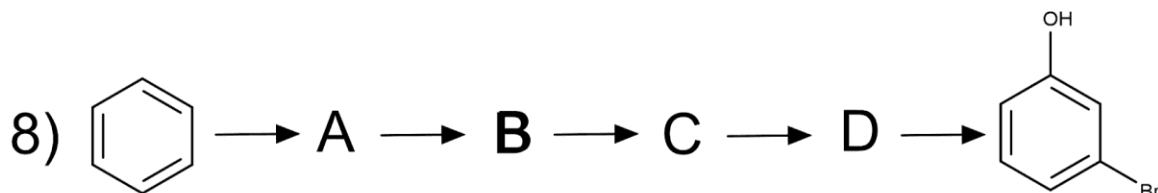
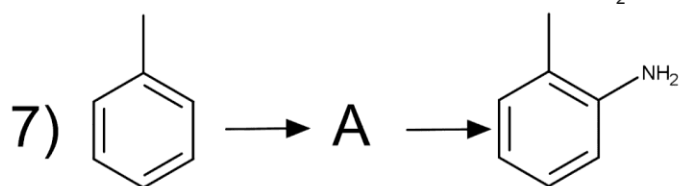
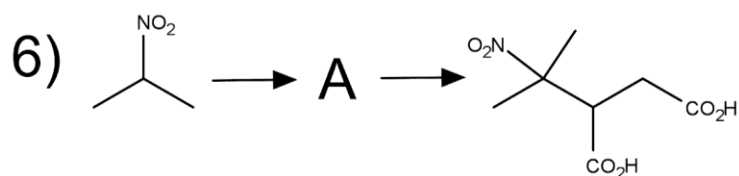
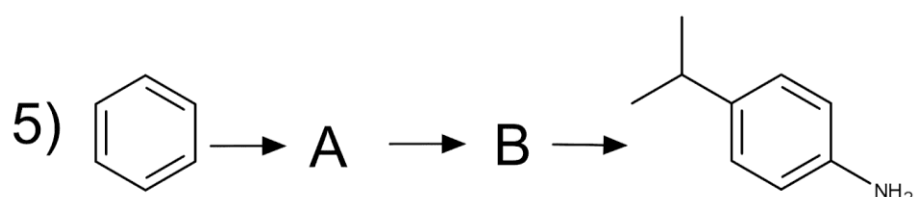
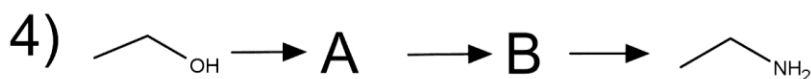
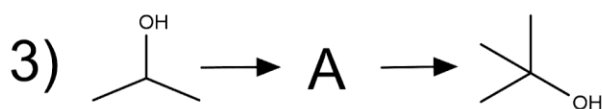
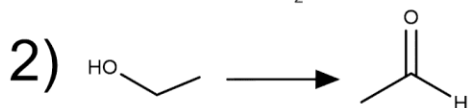
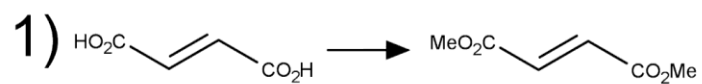
Write "Mitsunobu" under the corresponding arrow(-s) in your scheme.

Which of the syntheses use diazonium chemistry? **Underline** the corresponding numbers.

Draw the mechanism for the reaction step involving 1,4 addition (conjugate addition).

Draw the structural formula of the reaction product between **8)D** and benzyl chloride PhCH₂Cl.

The synthesis schemes for the 10 compounds Jonathan needs to synthesise



Reagent Bank:

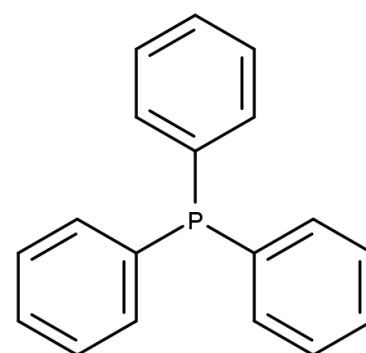
These chemicals can be found in Jonathan's reagent cabinet in the lab. You are allowed to use these chemicals or any substances produced by their reactions with other reagents from the Reagent Bank in order to do the required syntheses. A reagent may be used multiple times, not every of the reagents is required for Jonathan's syntheses (they might be needed for other experiments)

Inorganic:

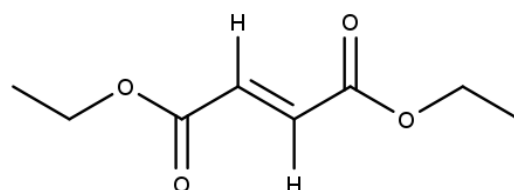
conc. H_2SO_4
conc. HCl
conc. HNO_3
 H_2O
aq. NH_3
 K_2CO_3
Mg metal
 NaBH_4
 AlCl_3
 NaNO_2
 BF_3 solution in diethyl ether
 Br_2
 $\text{K}_2\text{Cr}_2\text{O}_7$
 CuCl
 NaOH
Pd/C
a H_2 cylinder
 BaSO_4
 CuCN
 LiAlH_4
Sn metal
Na metal
Hydroxylamine NH_2OH

Organic:

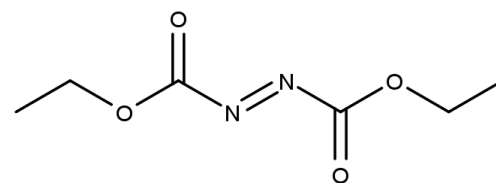
Ethanol EtOH
Isopropanol $i\text{-PrOH}$
Methanol MeOH
Pyridinium chlorochromate PCC
1-chloropropane $n\text{-PrCl}$
Methyl iodide MeI
Methylmagnesium bromide MeMgBr
Diethyl fumarate
Tetrahydrofuran THF
Dimethylsulfoxide DMSO
Ethylene glycol
Lithium diisopropylamide LDA
Toluene
Triphenylphosphine PPh_3



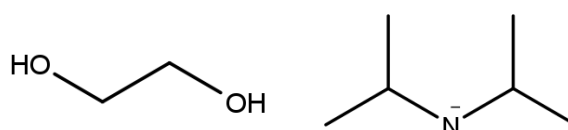
Triphenylphosphine



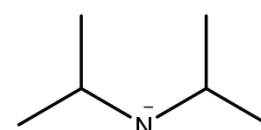
Diethyl fumarate



DEAD



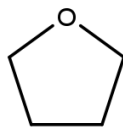
Ethylene glycol



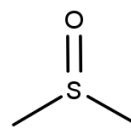
Li^+

LDA

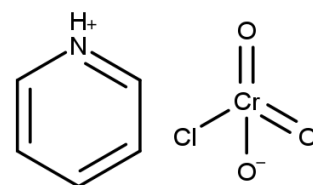
Diethyl azodicarboxylate DEAD
Butyronitrile n-PrCN



THF



DMSO

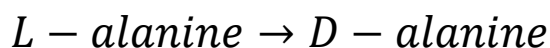


PCC

Part 3- Physical Chemistry

Problem 1. Kinetics of amino acid racemisation

The human body contains amino acids. All the α amino acids except glycine are chiral (around one of the C atoms the substituents are arranged in a particular fashion) and the human body contains enantiopure amino acids (consists only one enantiomer-way of arrangement of a chiral molecule). When amino acids are boiled, they tend to racemise (to become a 50:50 mixture of two enantiomers). The reaction of the racemisation of the L-alanine amino acid can be expressed as following:



The reaction is a first-order reaction accounting its rate. This means, the reaction rate in any given moment of the time is expressed by the following equation:

$$\frac{dA}{dt} = -k * A$$

where A is the concentration of the L-isomer at the given period of time t and k is the reaction rate constant.

*(This question will give you extra points to your olympiad if answered correctly, it is **not** included in the total grading because of the high difficulty)*

Derive the rate law for the reaction in a non-differential form. Use that if $t = 0$ $A = A_0$. Show your calculations.

The first order reaction law can be described using the same equation, but in another form without using differentials:

$$\frac{A}{A_0} = e^{-kt}$$

where A is the current concentration of L-alanine, A_0 is the beginning concentration of L-alanine, t is the time in seconds and k is the reaction rate constant.

Imagine the following situation:

On a chemical plant a worker was found dead in a pot of boiling water. In order to find out the exact time the victim was submerged into the pot the investigators decided to conduct an amino acid enantiomeric purity test. The L-enantiomeric excess appeared to be 12%.

Enantiomeric excess (ee) is calculated by the following formula:

$$(X_L - X_D) * 100\%$$

where $X(D)$ and $X(L)$ are the molar fractions of the L and D stereoisomers in the mixture.

First, the investigators carried out the following test: a sample of enantiopure L-alanine (enantiopure means that no D-isomer is present) was taken into a flask and boiled until the amino acid fully racemised. The time the process took was 7 hours and 24 minutes.

Calculate the reaction rate constant k . Provide your calculations. Express the answer in min^{-1} .

Calculate how long the accident victim was submerged in the boiling water. Provide your calculations.

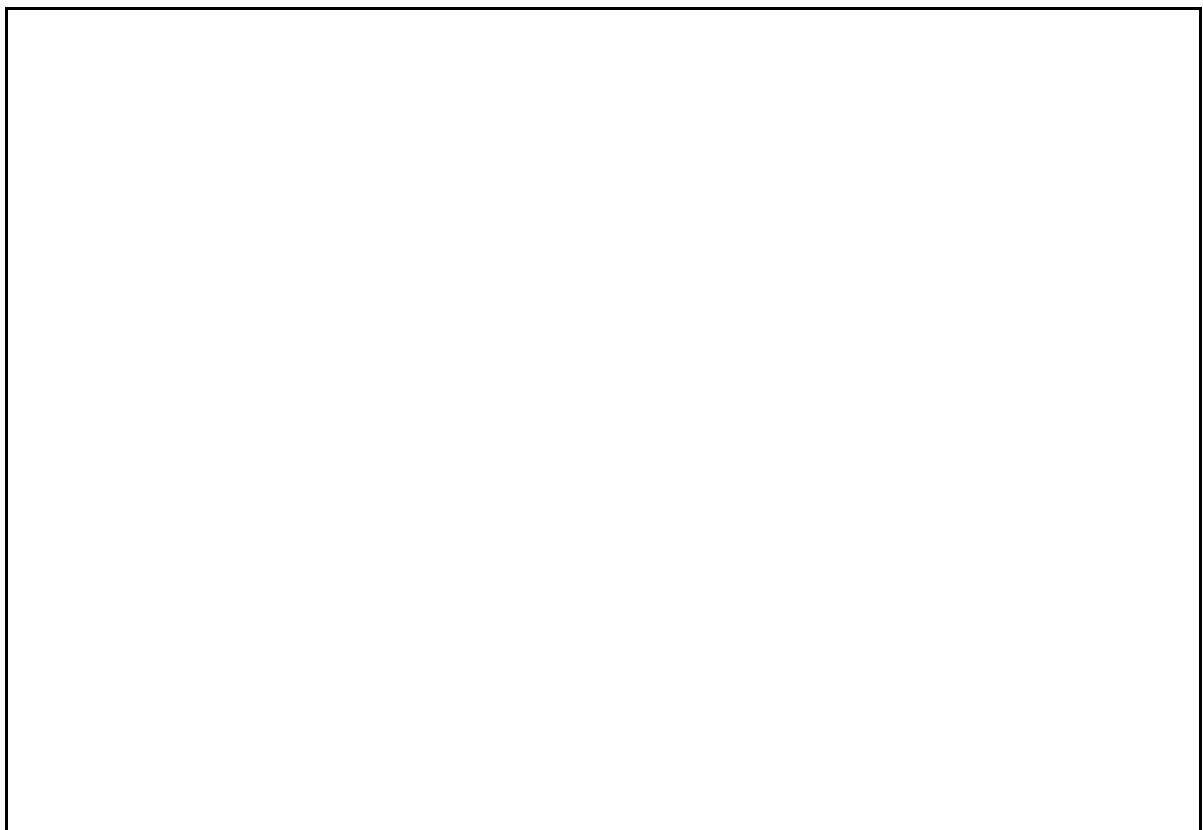


The reaction rate constant depends on temperature. The dependency was derived by Mr.Svante Arrhenius in 1889. It is originally formulated in a following way:

$$k = A * e^{-\frac{E_a}{RT}}$$

where A is a constant figure, E_a is the activation energy of the reaction in J/mol, R is the universal gas constant and T is the temperature in Kelvins.

Derive the equation for the calculation of the reaction activation energy if at $T = T_1$ $k = k_1$ and at $T = T_2$ $k = k_2$.



Calculate the activation energy in $\text{kJ}\cdot\text{mol}^{-1}$ for the racemisation reaction mentioned above if at $T_1=280\text{K}$ $k_1=0,075\text{ h}^{-1}$ and at $T_2=390\text{ K}$ $k_2=0,1\text{ h}^{-1}$ (*the k values do not correlate to earlier calculated values*).

Problem 2. Thermodynamics of burning fireworks

Chemistry enthusiast Ross was doing experiments with sulfur chemistry. He found out that the reaction of zinc and sulfur is highly exothermic and the heat produced is so big that the reaction product gets ejected out of the reaction mixture in the solid state. For the reaction $Zn(s) + S(s) = ZnS(s)$ at 600K the Gibbs energy of the reaction is equal to $-197.22 \text{ kJ}\cdot\text{mol}^{-1}$. The standard entropies of the reactants are listed in the table below:

Substance	$\Delta S, J \cdot mol^{-1} K^{-1}$
ZnS	57.7
Zn	41.6
S	31.8

Given that the Gibbs energy of the reaction can be expressed in the following manner: $\Delta G = \Delta H - T\Delta S$, where ΔG is the Gibbs free energy of the reaction, ΔS is the total entropy of the reaction, T is the temperature in kelvins and ΔH is the reaction enthalpy aka heat of the reaction.

Calculate the total entropy of the reaction above. Hint: the reaction entropy change is equal to the difference between the products' and the reactants' standard entropies.

Calculate the reaction enthalpy. Provide your calculations.

Ross decided to mix 1 kg of the stoichiometric sulfur and zinc mixture.

Calculate the concentration of all the reactants (in %) in the mixture as well as the total mass of each of them.

Ross placed the mixture outside, stepped back and started observing the reaction. He noticed that the reaction happens at a constant rate, and 40 g of the product is being produced every second.

We can assume that of the whole reaction heat (enthalpy) about 0.01% is converted into kinetic energy of the product molecules. **Assume** that all the product molecules have the same kinetic energy.

Calculate the mass of one product molecule. Report the answer in kilograms.

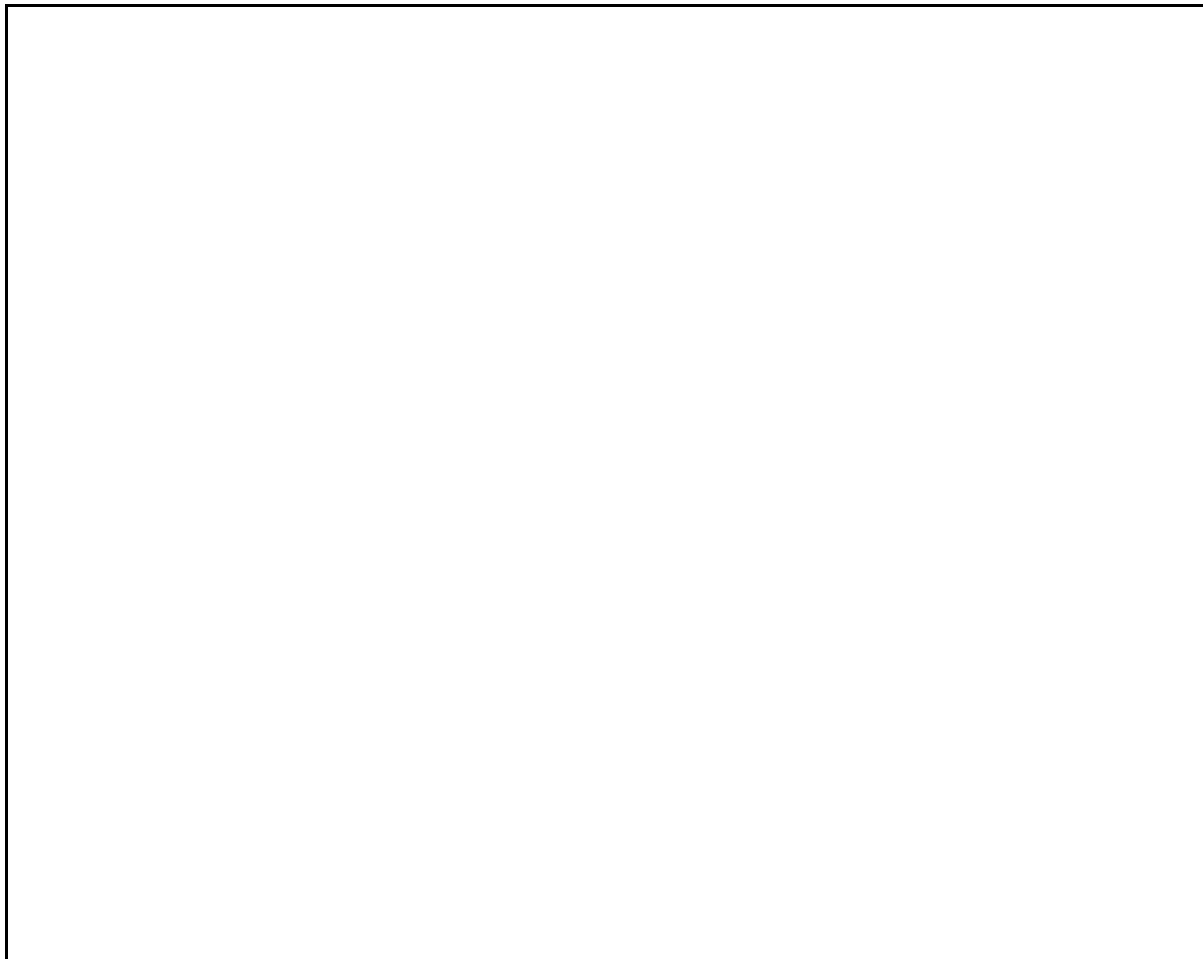
Calculate the kinetic energy of one product molecule. Report the answer in joules, provide calculations. If you failed to calculate the reaction enthalpy, use $\Delta H = -216.4 \text{ kJ/mol}$.

Ross also noticed that the reaction was quite spectacular so he decided to invite his friends little Ian, Agatha and Jonathan to his show where he would demonstrate the reaction to them. Although, the reaction mixture ejects hot zinc sulfide chunks, so the spectators would have to stand back in order not to get burnt by the reaction. Ross decided to put the chairs for the spectators on a safe distance, but not too far because then the reaction is not really well visible.

The maximum distance l the product particle can travel can be expressed by the following formula:

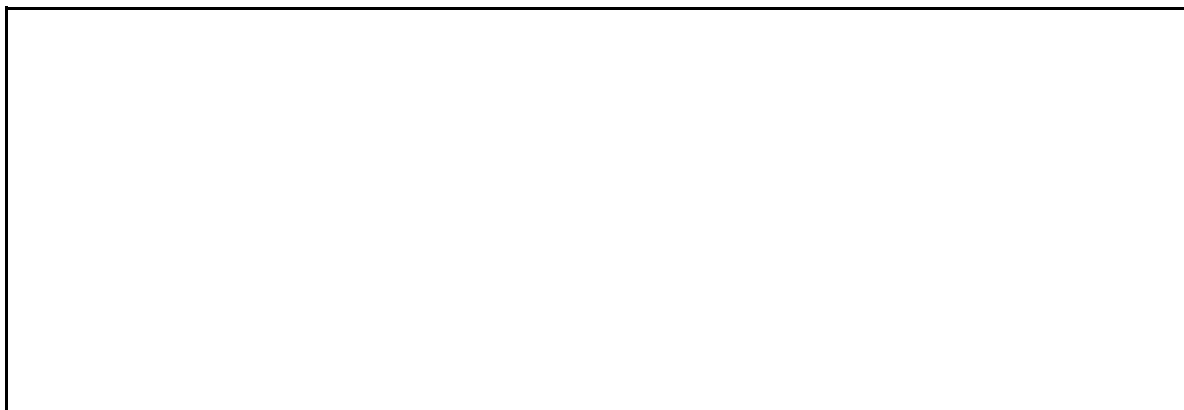
$l = \frac{2E}{mg}$ where E is the particle's kinetic energy (in J), m is the particle's mass (in kg) and $g = 9.8 \text{ m}\cdot\text{s}^{-2}$ is the free fall acceleration on Earth's surface.

Calculate the minimum safe distance L for the spectators to stand by if L must be at least 5 meters bigger than l to avoid particles with an increased speed hitting the observers.



Also, Ross decided to use the heat produced in the reaction to make him a cup of tea. He poured 1L of water into an iron pot and placed it directly over the reaction mixture. Assume that 40% of the total heat produced during the reaction is converted into heating the pot and water. The energy needed to heat up the pot and the water is calculated the following way: $E = nc\Delta T$ where c is the heat capacity of the substance, ΔT is the difference between the end temperature and the starting temperature (in Kelvins) and n is the amount of moles of the substance. Assume that the pot needs 900 J to be heated for 1K. $c(H_2O) = 75.6 J/(molK)$.

Calculate how much of Ross's mix will be needed to heat the water from 300K to boiling. If you failed to calculate the reaction enthalpy, use $\Delta H = -216.4 kJ/mol$.



Part 4- Meme Chemistry

Problem 1. Burette usage for non-scientific purposes

As you know, the burette is a very multifunctional tool in a laboratory. For example, it can be used not only for its intended purpose-titration, but also e.g. as a column for chromatography or as an alternative to using a graduated cylinder/pipette when the right piece of glassware is not available.

Suggest another method how to use the burette in the lab. The funniest suggestion will get extra points to their olympiad grade.

Problem 2. Sulfuric acid is not only a reagent

In the lab sulfuric acid is used for extremely diverse applications. Suggest a few ways to use concentrated 98% sulfuric acid except as a reagent. The funniest suggestion will get extra points to their olympiad grade.