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**
MnO_2	I_2	$Na_2S_2O_3$

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.

$2H_2O_2 \xrightarrow{MnO_2\ cat} 2H_2O + O_2$

$MnO_2 + 4HCl \rightarrow Cl_2 + 2H_2O + MnCl_2$

$MnO_2 + 2H_2 \xrightarrow{\Delta} Mn + 2H_2O$

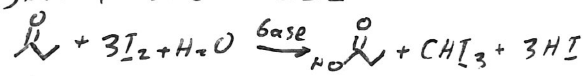
$Mn + 2HCl \rightarrow MnCl_2 + H_2$

$MnO_2 + 2KOH + KNO_3 \xrightarrow{\Delta} K_2MnO_4 + H_2O + KNO_2$

$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$

$8I_2 + 6KOH \rightarrow KIO_3 + 5KI_3 + 3H_2O$

$KIO_3 + 5KI_3 + 3H_2SO_4 \rightarrow 3K_2SO_4 + 3H_2O + 8I_2$



$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

$6NaOH + 4S \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$

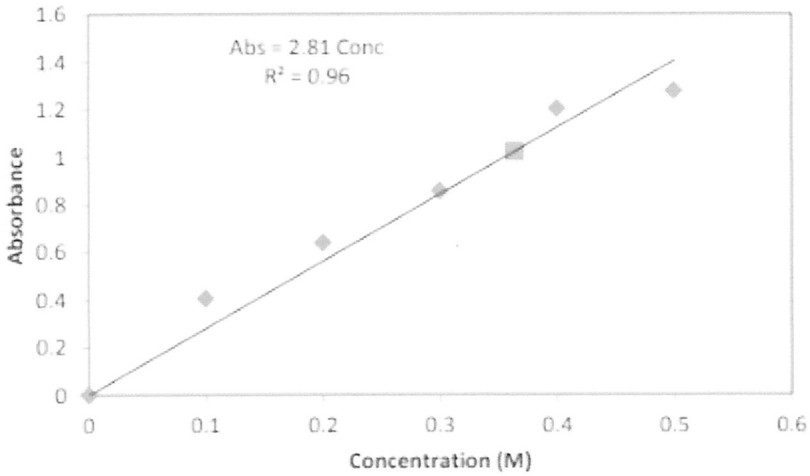
Problem 2. Anastasia and the copper shower

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:

$$A = \varepsilon c l$$

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.

$A = \varepsilon l c = 2,81c$

$\varepsilon l c = 2,81c$

$\varepsilon l = 2,81$

$\varepsilon = \frac{2,81}{3} = 0,94\ M^{-1}\ cm^{-1}$

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.

$l = 1mm = 0,1 cm$

$A = \varepsilon l c$

$c = \frac{A}{\varepsilon l}$

$c = \frac{0,04}{0,1 \cdot 0,94} = 0,4 M$

Problem 3. Impossible or reversible?

At one point, Danik 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:

$$C_{diamond} \rightarrow C_{graphite}$$

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 -2.9 kJ/mol. **Determine**, using the formula $\Delta G =- RT lnK$, the equilibrium constant for this reaction at 273 K.

$\Delta G = -RT \ln K$ $\quad R = 8{,}3\ J K^{-1} mol^{-1}$

$\ln K = \frac{\Delta G}{-RT}$ $\quad T = 273\ K$

$K = \exp\left(\frac{\Delta G}{-RT}\right)$

$K = \exp\left(\frac{2{,}9 \cdot 10^3}{8{,}3 \cdot 273}\right) = \exp(1{,}28) \approx 3{,}6$

The rate constant for the forward reaction is $6.93*10^{-81}s^{-1}$. **Determine** the half life of diamond conversion to graphite using the formula $t = ln(0.5)/ - k$

$t_{1/2} = \frac{\ln(0,5)}{-k}$ $-k \cdot t_{1/2} = \ln(0,5)$

$k = \frac{-\ln(0,5)}{t_{1/2}}$

$t_{1/2} = \frac{0,693}{6,93 \cdot 10^{-81}} = 10^{80}\ s$

Write the reaction equation for the reverse reaction.

$C_{graphite} \rightarrow C_{diamond}$

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

$K = \frac{kf}{kR}$ $K \cdot kR = kf$ $kR = \frac{kf}{K}$

$kR = \frac{6,93 \cdot 10^{-81}}{3,6} = 1,93 \cdot 10^{-81}\ s^{-1}$

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.

An ^1H NMR spectra which is empty gives Agatha the following info:
- No ^1H nuclei resonated => there are no hydrogen atoms in the molecule

A ^{13}C NMR spectra which is empty gives Agatha the following info:
- No ^{13}C nuclei resonated => there are no carbon atoms in the molecule

Agatha definitely knows that the molecule contains neither hydrogen nor carbon atoms.

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 2.05g the precipitate in a crucible at 1300K temperature for a few hours. The leftover solid with a mass of 1.44g 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 2.45g of the white powder decreased in mass by 1.24g.
What is the white powder's chemical formula? Explain your thoughts.

Na_2SO_3

- Reacts with aq. $Ba(NO_3)_2$ ⇒ anion is:
  - sulfate
  - carbonate
  - sulfite
  - phosphate

Out of whom only CO_3^{-2} and SO_3^{-2} produce a gas (CO_2, SO_2) on reaction w. dil HCl. Carbonate is not viable because of the NMR, sulfite is left. We check ourselves by calculating the gravimetric analysis of Ba^{2+} ppt decomposing

$BaCO_3 \rightarrow BaO + CO_2$ $n(BaCO_3) = n(BaO)$

$BaSO_3 \rightarrow BaO + SO_2$ $n(BaSO_3) = n(BaO)$

$\frac{2{,}05}{217} = n(BaSO_3)$ $\frac{2{,}05}{197} = n(BaCO_3)$ $\frac{1{,}44}{153} = n(BaO)$

$n(BaSO_3) = 0{,}009$ mol, $n(BaCO_3) = 0{,}01$ mol, $n(BaO) = 0{,}009$ mol

So, anion is sulfite

Cation is Na^+, K^+, Cs^+, Rb^+. Not NH_4^+ because of NMR.

Molar mass of salt: $80 + x$ — cation molar mass $\frac{2{,}45}{80+x} = \frac{1{,}24}{x+16}$

Of ppt after heating: $x + 16$

$x = 46$ g/mol = 2 Na

So, the white powder's molecular formula is Na_2SO_3, and the powder consists of sodium sulfite

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*)

$SO_3^{2-} + Ba^{2+} \rightarrow BaSO_3$

$BaSO_3 + 2H^+ \rightarrow Ba^{2+} + H_2O + SO_2$

$BaSO_3 \xrightarrow{\Delta} BaO + SO_2$

$BaO + H_2O \rightarrow Ba^{2+} + 2OH^-$

$SO_3^{2-} + Pb^{2+} \rightarrow PbSO_3$

$Na_2SO_3 \xrightarrow{\Delta} Na_2O + SO_2$

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.

Concentrated H_2SO_4 passivates iron, preventing further reaction

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. Solid **B** is blue, solid **A** is brown.

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

1 Iron does not passivate in concentrated hot H_2SO_4

2 There might also happen the following reaction with $CuSO_4$:
$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$, which also dissolves the bathtub because Cu is immediately dissolved back in conc. H_2SO_4

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

A $Fe_2(SO_4)_3$ iron (III) sulfate

B $CuSO_4$ copper(II) sulfate

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. $2Fe + 6H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3SO_2 + H_2O$
$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

$n(Fe_2(SO_4)_3) = 10$ mol 1 mol $Fe_2(SO_4)_3$ produced 3 mol SO_2 ⇒ 30 mol SO_2
$n(CuSO_4) = 50$ mol 1 mol $CuSO_4$ produced 1 mol SO_2 → 50 mol SO_2
Total = 50+30 = 80 mol SO_2

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.

$pV = nRT$

$T = 207\ C = 207 + 273 = 480\ K$

$p = 1300\ mmHg = 173\ kPa$

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

$V = \frac{80 \cdot 8{,}314 \cdot 480}{173 \cdot 10^3} = 1{,}85\ m^3$

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 poured[1] 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)*

The reaction is highly exotermic
When heated well enough, NaK alloy (and Na metal) reacts with oxygen in air and explodes due to the exothermic reactions:

$2Na + O_2 \rightarrow 2NaO_2$

$K + O_2 \rightarrow KO_2$

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.

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

[1] Sodium-potassium alloy is a liquid at room temperature

At STP 1mol of each gas occupies 22,4 L

So, n(gas) = $\frac{3332}{22,4}$ = 148,75 mol

$Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2$

$K + H_2O \rightarrow KOH + \frac{1}{2}H_2$

n(Na+K) = 148,75·2 = 297,5 mol

n(Na) - x   n(K) - y

x + y = 297,5

23x + 39y = 10 000

x = 100,16 mol   => m(Na) = 100,16·23 = 2304 g

y = 197,34 mol   m(K) = 197,34·39   7696 g

w(Na) = 23,04%   w(K) = 76,96%

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.

n(NaOH) = 100,16 mol

n(KOH) = 197,34 mol

n(OH) = 297,5 mol

The pond is 595 m^3 of water or $595 \cdot 10^3$ L

$[OH^-] = \frac{n(OH^-)}{V}$

$[OH^-] = \frac{297,5}{595000} = 500 \cdot 10^{-6}$ M

$[H^+] \cdot [OH^-] = K_w$ $K_w = 10^{-14}$

$[H^+] \cdot 500 \cdot 10^{-6} = 10^{-14}$

$[H^+] = 2 \cdot 10^{-11}$

pH = -log [H^+]

pH = -log ($2 \cdot 10^{-11}$) = 10,7

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, 8L (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 1.8 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.

Ag

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

$Ag^+ + \bar{e} \rightarrow Ag^0$ Cathode

$2H_2O - 4\bar{e} \rightarrow O_2 + 4H^+$ Anode

$4Ag^+ + 2H_2O \rightarrow 4Ag + O_2 + 4H^+$ net reaction

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)

$Au + 4HCl + HNO_3 \rightarrow H[AuCl_4] + NO + 2H_2O$

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

$[AuCl_4]^- + 3Fe^{2+} \rightarrow 3Fe^{3+} + Au + 4Cl^-$

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

$I = \frac{q}{t}$ $\quad n = \frac{It}{Fz}$ $\quad Ag^+ + e \rightarrow Ag^0$ $\quad z = 1$

$q = It$ $\quad m = n \cdot M = \frac{ItM}{Fz}$ $\quad I = 5A$ $\quad t = 4438\ s$

$M(Ag) = 108\ g/mol$

$\frac{q}{zF} = n$

$m(Ag) = \frac{5 \cdot 4438 \cdot 108}{96485} = 24,8\ g$

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

1. The medal contains 1,8 g Au
2. The medal contains 24,8 g Ag
3. $Fe + 2HCl \rightarrow FeCl_2 + H_2$

   $n(Fe) = \frac{8}{22,4} = 0,357\ mol$

   $m(Fe) = 0,357 \cdot 56 = 20\ g$

   the medal contains 20 g Fe
4. The medal contains $60 - 20 - 1,8 - 24,8 = 13,4$ g Cu

Total mass of the medal = 60 g

$w(Fe) = 33,3\%$

$w(Au) = 3\%$

$w(Ag) = 41,3\%$

$w(Cu) = 22,3\%$

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.

F 1. Potassium perchlorate is also called Bertolle's salt.

T 2. When potassium iodide is mixed with bromine, a dark brown precipitate of iodine forms.

F 3. Iodine never melts at atmospheric pressure, it sublimes.

F 4. A compound with the formula ClF_5 can not exist.

T 5. Sodium hypochlorite is a very strong disinfectant.

T 6. Bleach consists of sodium, chlorine and oxygen atoms.

F 7. Bromine is the only element that is liquid at 273K.

F 8. When water and chlorine gas react together, water oxidises the chlorine atoms to chloride ions.

F 9. When liquid potassium chloride is electrolyzed, on the cathode chlorine gas is formed.

T 10. Iodine reacts with acetone in basic conditions and produces a yellow precipitate.

T 11. Potassium iodide in solution reacts with iodine to form a complex.

F 12. The molecule with the formula CCl_4 is called chloroform.

T 13. When sodium hypochlorite reacts with hydrogen chloride, hypochlorite ions oxidise the chloride ions.

F 14. Hydrogen chloride can be oxidised by iodine to form chlorine and hydrogen iodide.

F 15. Chloride is a good bidentate ligand.

T 16. When methane is mixed with chlorine gas and treated with UV light, ethane forms.

F 17. Sodium chlorate is used as table salt.

F 18. The hypobromous acid is unstable and quickly disproportionates into perbromic acid and hydrogen bromide at room temperature.

F 19. If you mix 50g of NaOCl with 40g of HCl 10 L (at STP) of gas is produced.

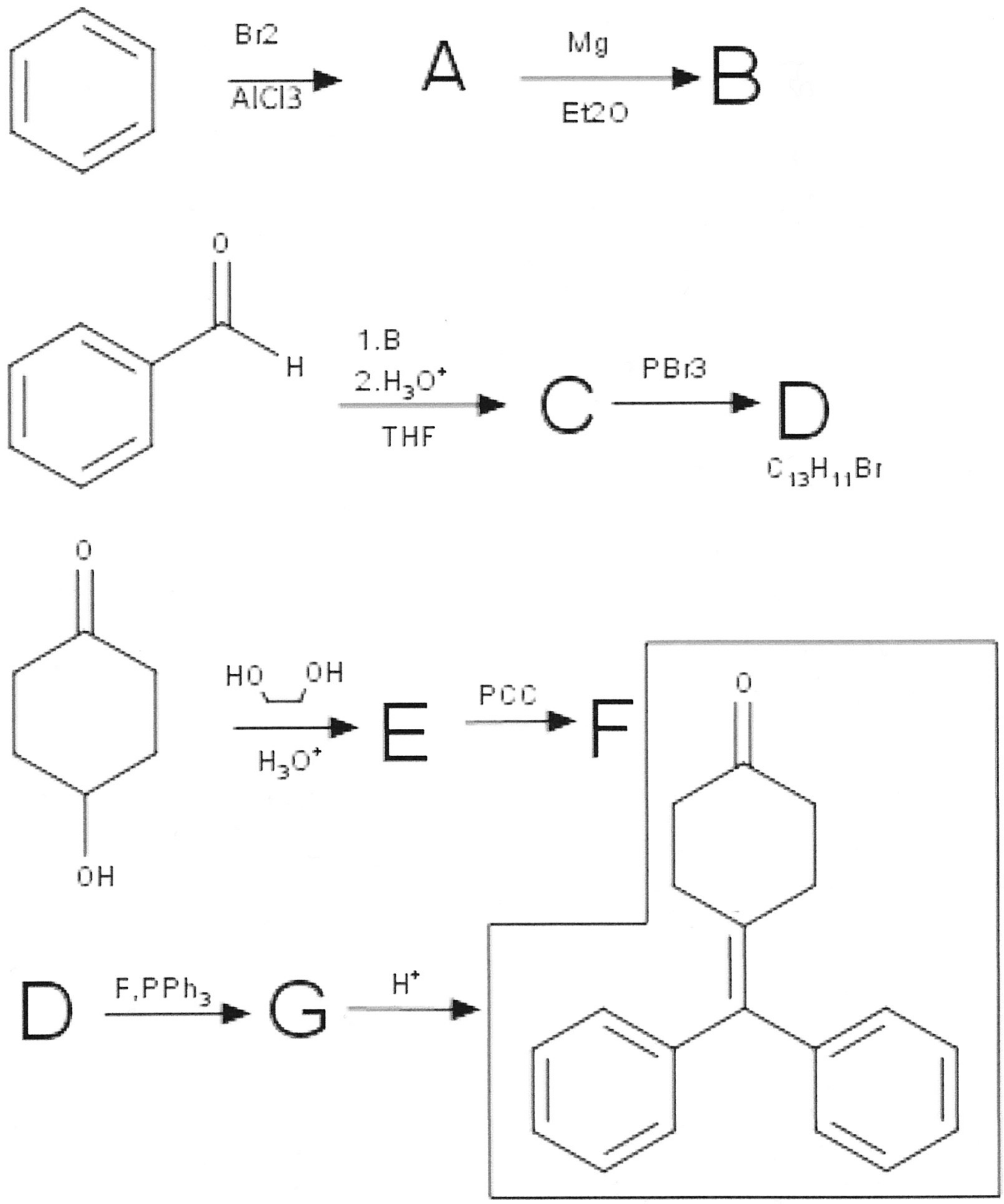
T 20. When fluorine gets mixed with water, the fluorine atoms get reduced.

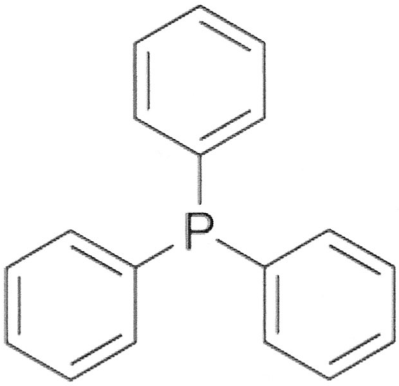
Write T or F before the phase number, T for correct statements, F for wrong ones.

Part 2- Organic Chemistry

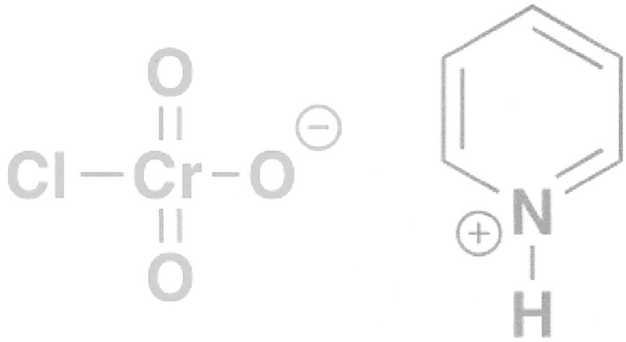
Problem 1. Synthesizing dreams

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.



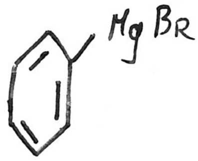
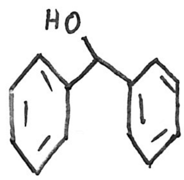
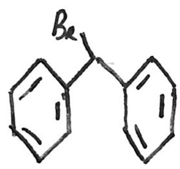


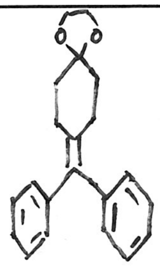
PPh$_3$



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?

It makes an acetal prot. group to prevent the formation of a diene

Is the final product aromatical?

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

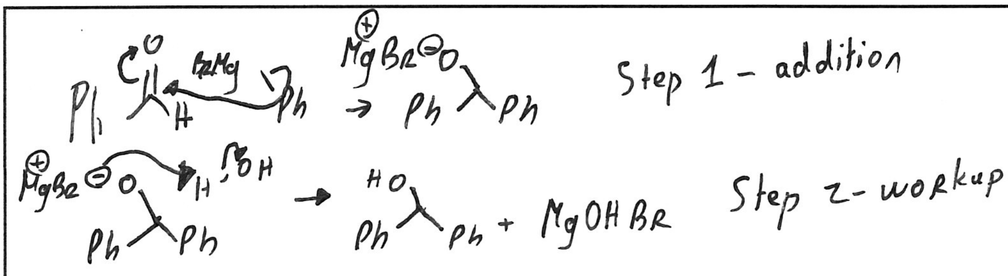
Which mechanism does the **benzene=>A** step follow?

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

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

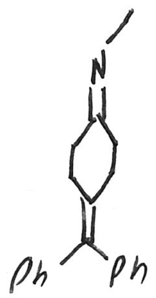
a)as a catalyst b)to break the C-H bond in benzene c)to introduce only one bromine

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.

Aniline

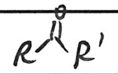
Which reaction mechanism does the **A+NaNH₂** reaction follow?

a)S_N1 b)S_N2 c)benzyne mechanism d)S_NAr

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
alcohol -OH	carbonyl group, ketone 

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?

No, cyclohexane is not planar, there is rotation along C-Ph

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

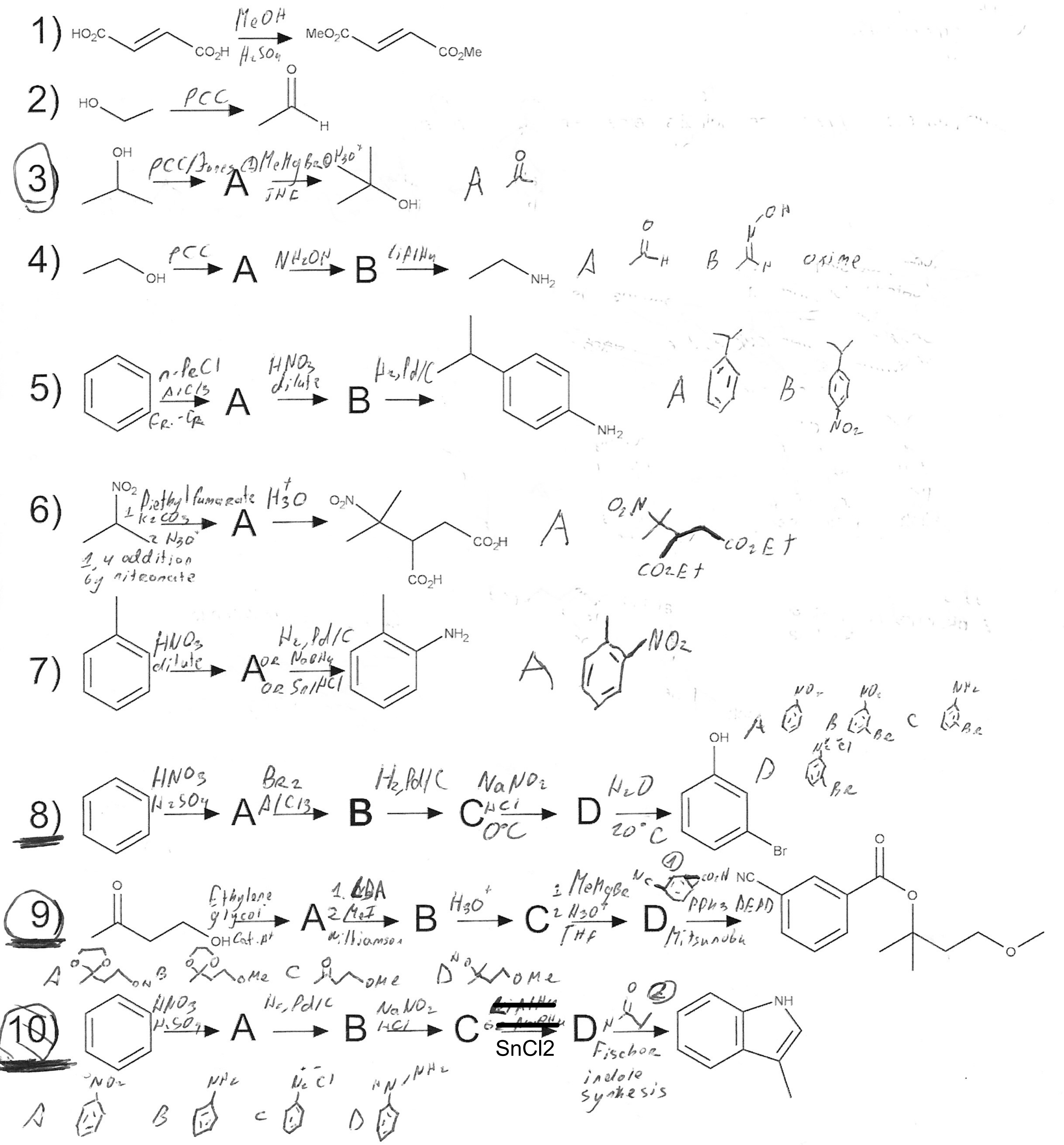
What is the name of compound **C**?

Diphenyl methanol

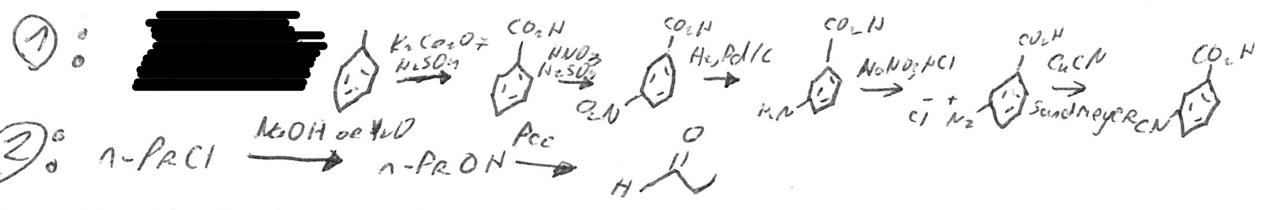
Problem 2. You'd better not trust the IT department

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 C_2H_5OH)
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 all the 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 $PhCH_2Cl$.

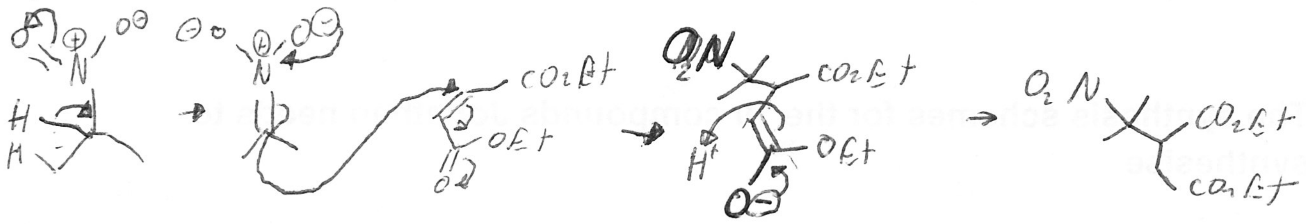
The synthesis schemes for the 10 compounds Jonathan needs to synthesise



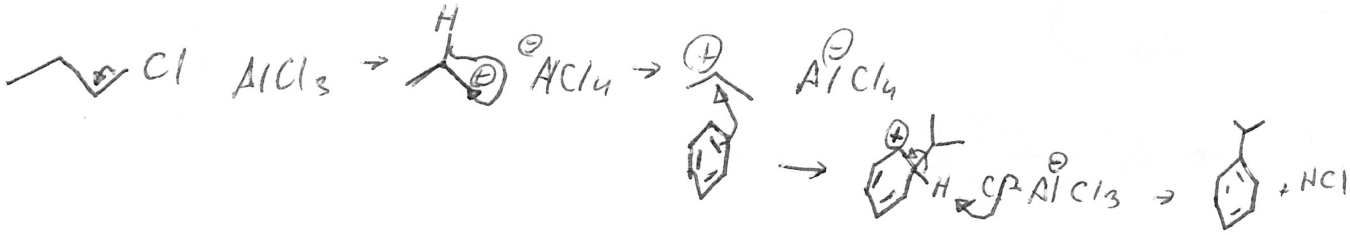
[redacted]



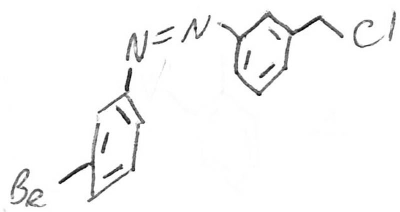
1, 4 addition:



5th synthesis:



Product:



azo coupling

, -CH_2Cl is meta -directing as an EWG

Reagent Bank:

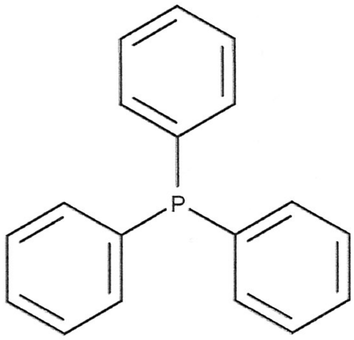
These chemicals can be found in Jonathan's reagent cabinet in the lab. You are allowed to use these chemicals or any substances produced by their reactions with other reagents from the Reagent Bank in order to do the required syntheses. A reagent may be used multiple times, not every of the reagents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

Inorganic:

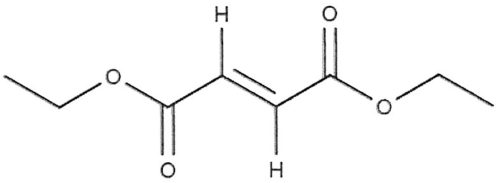
- conc.H_2SO_4
- conc.HCl
- conc.HNO_3
- H_2O
- aq. NH_3
- K_2CO_3
- Mg metal
- $NaBH_4$
- $AlCl_3$
- $NaNO_2$
- BF_3 solution in diethyl ether
- Br_2
- $K_2Cr_2O_7$
- CuCl
- NaOH
- Pd/C
- a H_2 cylinder
- $BaSO_4$
- CuCN
- $LiAlH_4$
- Sn metal
- Na metal
- Hydroxylamine NH_2OH

Organic:

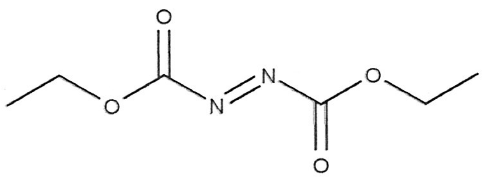
- Ethanol EtOH
- Isopropanol i-PrOH
- Methanol MeOH
- Pyridinium chlorochromate PCC
- 1-chloropropane n-PrCl
- Methyl iodide MeI
- Methylmagnesium bromide MeMgBr
- Diethyl fumarate
- Tetrahydrofuran THF
- Dimethylsulfoxide DMSO
- Ethylene glycol
- Lithium diisopropylamide LDA
- Benzene
- Triphenylphosphine PPh_3
- Diethyl azodicarboxylate DEAD
- Butyronitrile n-PrCN



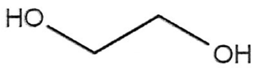
Triphenylphosphine



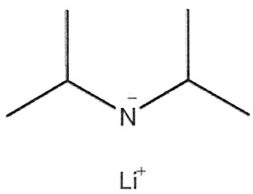
Diethyl fumarate



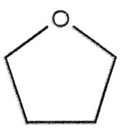
DEAD



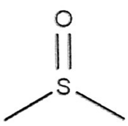
Ethylene glycol



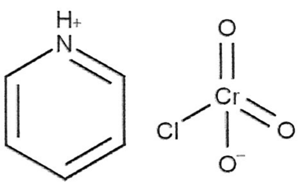
LDA



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:

$$L - alanine \rightarrow D - alanine$$

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.

$\frac{dA}{dt} = -k \cdot A$ $\quad dA = -k \cdot A \cdot dt$ $\quad \frac{dA}{A} = -k \cdot dt$

Integrate both parts of the equation:

$\int \frac{dA}{A} = -k \cdot \int dt$

$\int \frac{1}{A} dA = -kt$

$\ln A + C = -kt$

At $t = 0$ $A = A_0$, so:

$\ln A_0 + C = 0$

$-\ln A_0 = C$

$\ln A - \ln A_0 = -kt$

$\ln\left(\frac{A}{A_0}\right) = -kt$

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

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

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

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}.

Let A_0 be the starting concentration of L-alanine.
When racemated, concentration of L-alanine is $\frac{1}{2} A_0$

$$\frac{0{,}5\ A_0}{A_0} = e^{-kt}$$

$$\ln(0{,}5) = -kt$$

$$k = \frac{-\ln(0{,}5)}{t} \qquad t = 7h\ 24min = 7 \cdot 60 + 24 = 444\ min$$

$$k = 1{,}56 \cdot 10^{-3}\ min^{-1}$$

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

$ee = 12\%$ $x - c(L)$ $y(D)$

$x - y = 12$

$x + y = 100$

$2x = 112$

$x = 56\%$

A - start conc. of L-alanine

end. conc. of L-alanine is 0,56 A

$$\left(\frac{0,56A}{A}\right) = e^{-kt}$$

$$\ln(0,56) = -kt$$

$$t = \frac{\ln(0,56)}{-k}$$

$$t = 372 \text{ min}$$

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:

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

where A is a constant figure, Ea 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 $T = T1$ $k = k1$ and at $T = T2$ $k = k2$.

$k_1 = A \cdot \exp\left(\frac{-Ea}{RT_1}\right)$ ① $k_2 = A \cdot \exp\left(\frac{-Ea}{RT_2}\right)$ ②

Divide eq. ② by eq. ①:

$$\frac{k_2}{k_1} = \frac{\exp\left(\frac{-Ea}{RT_2}\right)}{\exp\left(\frac{-Ea}{RT_1}\right)}$$

$$\frac{k_2}{k_1} = \exp\left(-\frac{Ea}{RT_2} + \frac{Ea}{RT_1}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\frac{RT_1T_2}{T_2 - T_1} \ln\left(\frac{k_2}{k_1}\right) = Ea$$

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

$$E_a = \ln\left(\frac{k_2}{k_1}\right) \cdot \frac{RT_1T_2}{T_2 - T_1}$$

$$E_a = \ln\left(\frac{0{,}1}{0{,}075}\right) \cdot \frac{8{,}314 \cdot 280 \cdot 390}{390 - 280} = 0{,}29 \cdot 8254 = 2393 \text{ J mol}^{-1}$$

$$= 2{,}4 \text{ kJ mol}^{-1}$$

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 kJ*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.

$\Delta S = 57,7 - 41,6 - 31,8 = -15,7\ J \cdot mol^{-1} \cdot K^{-1}$

Calculate the reaction enthalpy. Provide your calculations.

$\Delta G + T\Delta S = \Delta H$
$\Delta H = -197220 - 600 \cdot 15,7 = -206640\ J/mol = -206,64\ kJ\ mol^{-1}$

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 needs 1 mol of Zn per 1 mol of S.
It comes to a mass proportion of 65 g Zn : 32 g S
$w(S) = \frac{32}{32+65} = 33\%$ $w(Zn) = \frac{65}{97} = 67\%$
For 1000 g of the mixture Ross needs 330 g S and 670 g Zn.

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.

$M(ZnS\ mol.) = \frac{M(ZnS)}{N_A} = \frac{97}{6{,}02\cdot10^{23}} = 1{,}6\cdot10^{-22}\ g = 1{,}6\cdot10^{-25}\ kg$

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

Every second, 40 g of ZnS are produced.
These are $\frac{40}{97}\cdot 6{,}02\cdot10^{23} = 2{,}48\cdot10^{23}$ molecules.
40g of ZnS correlates to $\frac{40}{97} = 0{,}412$ mol
Per 1 mol of ZnS 206,64 kJ of heat are produced, per 0,412
$0{,}412\cdot 206{,}64 = 85{,}14$ kJ are produced.
Of those 85,14 kJ 0,01% become kinetic energy of ZnS molecules.
This is $85140 \cdot 0{,}0001 = 8{,}514$ J
Thus, the kinetic energy of each ZnS molecule is $\frac{8{,}514}{2{,}48\cdot10^{23}} = 3{,}43\cdot10^{-23}$ J

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 m*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.

Fiast, let us calculate l.

$l = \frac{1E}{mg} = \frac{20 \cdot 3{,}43 \cdot 10^{-23}}{9{,}8 \cdot 1{,}6 \cdot 10^{-25}} = 43{,}75\ m$

L - the safe distance must be at least 5 m moae than l, thus $L_{min} = 43{,}75 + 5 = 48{,}75\ m$

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: $E = n$[redacted]$c\Delta T$ [redacted] 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. $c(H2O) = 75.6\ J/(molK)$.

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

Watea boils at 373 K, so the ΔT is equal to $373 - 300 = 73\ K$

To heat up the pot, $900 \cdot 73 = 65{,}7\ kJ$ of heat are needed

1 L of watea is $\frac{1000}{18} = 55{,}6$ mol

Thus, $E = 55{,}6 \cdot 75{,}6 \cdot 73 = 306{,}85\ kJ$ of heat

$E_{total} = 306{,}85 + 65{,}7 = 372{,}55\ kJ$

To pRovide $372{,}55\ kJ$ of heat, $\frac{372{,}55}{0{,}4} = 931{,}375\ kJ$ of buaned l_1+5 aae needed

To get this heat, $\frac{931{,}375}{206{,}64} = 4{,}5$ mol of the mixtuae need to be coasumed. This coaaelates to $4{,}5 \cdot 97 = 436{,}5\ g$ of the mixtuae