Code: USA-

Name:

Team Alpha Moo
Mock Camp Test

Theoretical Problems
Exam 2

You may want to consult the readme document so that you can read the protocols for how exams at camp are typically carried out: https://docs.google.com/document/d/1hV-thZ-qkU33DEkqGt-le5SVOTgkNRfHpgEjkTeNHyY/edit?usp=sharing

Instructions

- Write your name only on the cover sheet of the test
- Write your code number on each page (pages with no code will not be graded!)
- You have 2 hours to work on the problems
- Use only the pen and calculator (TI-30XIIS) provided
- All results should be written in the appropriate boxes. If you need extra space you may draw another box on the same page or on the backside of a different page and write a note telling the grader to refer to the backside of that page.
- Box your answers
- You may use the backsides of the sheets for scratch paper. You will not be provided with separate pieces of scratch paper.

Problem 1
Ammonia Synthesis Kinetics

9% of the total

1a	1b	Total	%
4	10	14	9

A possible ion–molecule reaction mechanism for the synthesis of ammonia in interstellar gas clouds is shown below

$$
\begin{array}{llll}
N^+ + H_2 & \longrightarrow & NH^+ + H & k_1 \\
NH^+ + H_2 & \longrightarrow & NH_2^+ + H & k_2 \\
NH_2^+ + H_2 & \longrightarrow & NH_3^+ + H & k_3 \\
NH_3^+ + H_2 & \longrightarrow & NH_4^+ + H & k_4 \\
NH_4^+ + e^- & \longrightarrow & NH_3 + H & k_5 \\
NH_4^+ + e^- & \longrightarrow & NH_2 + 2H & k_6
\end{array}
$$

(a) Use the steady state approximation to derive equations for the concentrations of the intermediates NH^+ , NH_2^+ , NH_3^+ and NH_4^+ in terms of the reactant concentrations $[N^+]$, $[H_2]$ and $[e^-]$. Treat the electrons as you would any other reactant.

(b) Determine the rate law for the production of NH_3 as a function of $[N^+]$ and $[H_2]$. Give an expression for the overall rate constant k in terms of the rate constants for the elementary steps, k_1 to k_6.

Problem 2
Bismuth Determination

14% of the total

2a		2b	2c	2d	2e	2f	2g	h	i	j	k	l	Total	%
i	ii	1	1	3	4	1	3	2	3	5	2	1	29	14
2	1													

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy.

(a) As an example, we shall consider the method used for the determination of microscopic amounts of bismuth. In 1927 German chemist Berg suggested to precipitate bismuth as a practically insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate $[C_9H_6(OH)NH][BiI_4]$ (M_r = 862.7).

(i) Draw the structural formulae of the cation and anion of this salt.

(ii) What is the oxidation state of Bi atom in this compound?

(b) Evaluate the smallest mass of bismuth (in mg), which can be determined reliably by Berg method, if the smallest mass of precipitate which can be reliably measured is 50.0 mg.

For the determination of trace amounts of bismuth R. Belcher and co-workers from Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

Step 1: To a given small amount (≈ 2 cm^3) of cold acidified solution containing trace amounts of Bi^{3+} 50 mg of potassium hexathiocyanatochromate(III) ($K_3[Cr(SCN)_6]$) is added in the cold, that leads to practically quantitative precipitation of bismuth.

(c) Write a balanced net ionic equation of this reaction.

Step 2: The precipitate is filtered off, washed by cold water, and treated with 5 cm^3 of 10 % solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate transforms into the precipitate of oxobismuth(III) carbonate $(BiO)_2CO_3$ with liberation of hexathiocyanatochromate(III) ions into solution.

(d) Write a balanced net ionic equation of this reaction.

Step 3: To the slightly acidified filtrate transferred to a separatory funnel 0.5 cm^3 of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidizes the ligand of the complex ion to ICN and sulphate ion.

(e) Write a balanced net ionic equation of this reaction.

Step 4: Upon 5 minutes 4 cm^3 of 2 M H_2SO_4 solution are added to the mixture. The acidification leads to the reaction of comproportionation with the evolution of molecular iodine.

(f) Write a balanced net ionic equation of the reaction occurred on acidification.

Step 5: Iodine is quantitatively extracted by 4 portions of chloroform. Aqueous layer is transferred to a flask, to which 1 cm^3 of bromine water is added, and the mixture is mixed for 5 minutes.

(g) Write the balanced net ionic equations of the reactions occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give BrCN, and iodide is oxidized into IO_3^-.

Step 6: To eliminate an excess of molecular bromine 3 cm^3 of 90 % methanoic acid is added to the mixture.

(h) Write a balanced net ionic equation of this reaction.

Step 7: To the slightly acidic solution an excess (1.5 g) of potassium iodide is added.

(i) Write the balanced net ionic equations of the reactions occurred upon the addition of KI, taking into consideration that iodide reacts with BrCN in a similar manner as with ICN to form molecular iodine.

Step 8: The resulting solution is titrated by a standard 0.00200 M $Na_2S_2O_3$ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

(j) How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

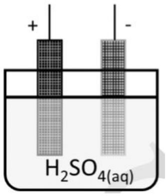
(k) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm^3 of standard 0.00200 M $Na_2S_2O_3$ solution)?

(l) By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

Problem 3
Lead Acid Batteries **14% of the total**

3a	3b	3c	3d	3e	3f	3g	Total	%
2	2		1	3	1	3		14

Conventional lead acid batteries used in cars and inverters are the most common rechargeable batteries in the market. A rechargeable lead acid cell consists of a positive electrode of Pb(s)/PbO_2(s), and a negative electrode of Pb(s), both immersed in aqueous H_2SO_4 electrolyte.



Standard electrode potentials for some half-cell reactions at 298 K are given below.

Half-Cell Reaction	E° (V)
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.69 V
$PbO_2(s) + 4\,H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2\,H_2O(l)$	+1.46 V
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13 V
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	-0.36 V

(a) Write the half-cell reactions that take place at cathode and at anode in above cell during discharge at 298 K. Write the overall discharge reaction and calculate the E° of this cell.

Molar Enthalpies of formation at 298 K of some species are given below.

Species	ΔH°_f (kJ mol^{-1})
$PbO_{2\,(s)}$	-277.4
$H_2O_{(l)}$	-285.8
$Pb^{2+}_{(aq)}$	1.6
$SO_4^{2-}{}_{(aq)}$	-909.3
$PbSO_{4(s)}$	-920.0

(b) Calculate the standard enthalpy change and standard Gibbs energy change for the overall discharge reaction of the cell in (a).

In a galvanic cell, the chemical energy released during the discharge reaction drives the electrical work. The Gibbs energy change of the discharge reaction represents the maximum electrical work $w_{max(el)}$ that can be extracted from the cell during discharge.

$w_{max(el)} = -\Delta G°_{rxn}$

Maximum work is obtained when the cell is operated reversibly, i.e., at a very low current. Assume that the cell is designed to exchange heat with the surrounding to prevent overheating or overcooling.

(c)For reversible operation of the cell at 298 K and all species in the cell in their standard states

(i) determine the amount of heat absorbed by the cell from the surrounding per mole of reaction as per the cell equation in 1.1.

(ii) what fraction of $w_{max(el)}$ is obtained from the heat exchanged reversibly with the surroundings?

The concentration c of a species in a solution is related to its activity a as a = γ × c, where γ is the activity coefficient. For highly concentrated solutions, the reaction quotient Q must be expressed in terms of activities of the species (i.e., $\gamma \neq 1$).

In commercial lead-acid batteries, highly concentrated H2SO4 (aq.) is used. Conventionally, the liquid and solid components in a chemical reaction are assumed to be in their 'standard states' with activity as 1. However, due to the high concentration of sulfuric acid in the electrolyte, the activity of water also cannot be taken as 1

(d) For the discharge reaction of cell in (a), write the expression for the cell EMF in terms of activities of the species involved in the reaction. Consider H_2SO_4 (aq.) to be completely dissociated and assume that only solids are in their standard states.

The lead-acid cell is considered to be discharged when the current that can be drawn from it decreases below a certain value. Discharge is also accompanied by a decrease in H2SO4 concentration. Activities of water and products of activities of relevant sulfuric acid species at 298 K in a lead acid cell are listed below at two concentrations of sulfuric acid.

No.	H_2SO_4 Molality (m)	a_{H2O}	$(a_{H+})^2(a_{SO42-})$
1	1.00	0.9618	0.0018
2	5.00	0.7032	0.8847

(e)Assuming the discharged and charged states correspond to 1.00 molal and 5.00 molal H_2SO_4, respectively, find the drop in the cell EMF values when it is discharged at 298 K.

Following are certain facts about the cell in Fig. 1.

(i) $PbSO_4$(s) predominantly deposits on the electrodes and not in other parts of the cell.

(ii) $PbSO_4$(s) deposits on both the electrodes.

(iii) Resistivity of $PbSO_4$(s) deposits (3×10^9 Ω cm) is much higher than that of PbO_2(s) (2×10^{-4} Ω cm).

(iv) Resistivity of PbO_2(s) (2×10^{-4} Ω cm) is close to that of Pb(s) (0.2×10^{-4} Ω cm).

(f) Which of the above facts makes the cell rechargeable? (Write Statement number(s) i - iv, as applicable)

A different type of lead-based galvanic cell is given below. This cell has methane-sulphonic acid in which Pb^{2+} has high solubility. The electrolyte consists of Pb^{2+} ions dissolved in aqueous CH_3SO_3H in a cell having two inert electrodes. When external power supply is connected to this cell, Pb^{2+} ions are reduced at one electrode and oxidized at the other electrode, with the products depositing on the respective electrodes.

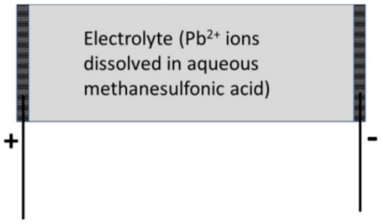


Figure 2: Simplified schematic of a lead acid cell based on methanesulphonic acid

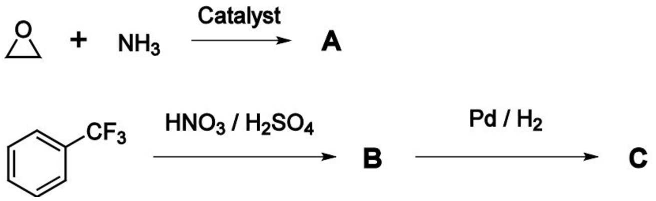
(g) Write the half-cell reactions that take place at cathode and at anode in the cell in Fig. 2 during discharge at 298 K. Write the overall discharge reaction and calculate the E° of this cell.

Problem 4
Flibanserin

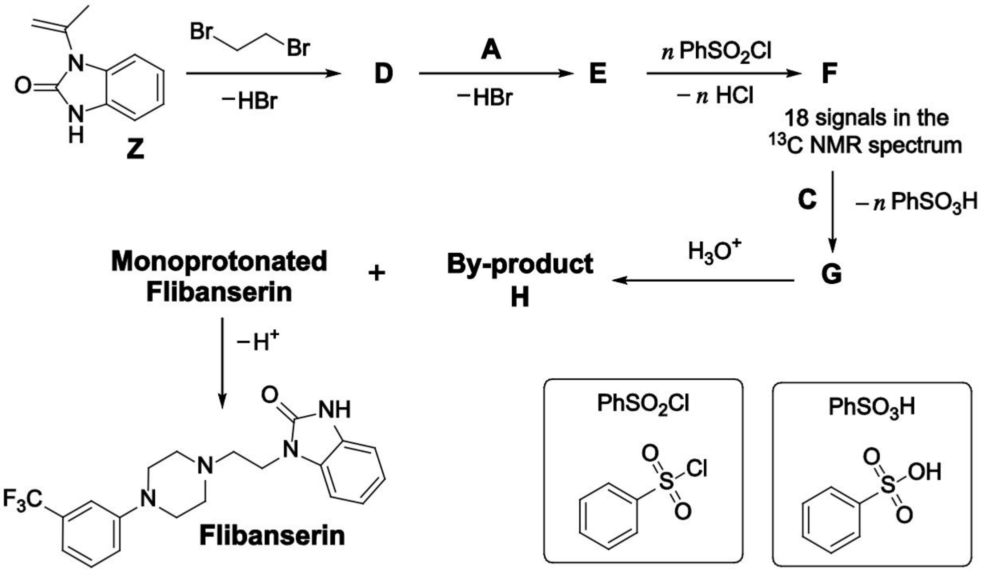
7% of the total

4a	4b	Total	%
15	7	22	7

In the synthesis of the drug Flibanserin, two precursor molecules **A** and **C** were first synthesised as shown in the scheme below.



Following is the full synthetic scheme of Flibanserin

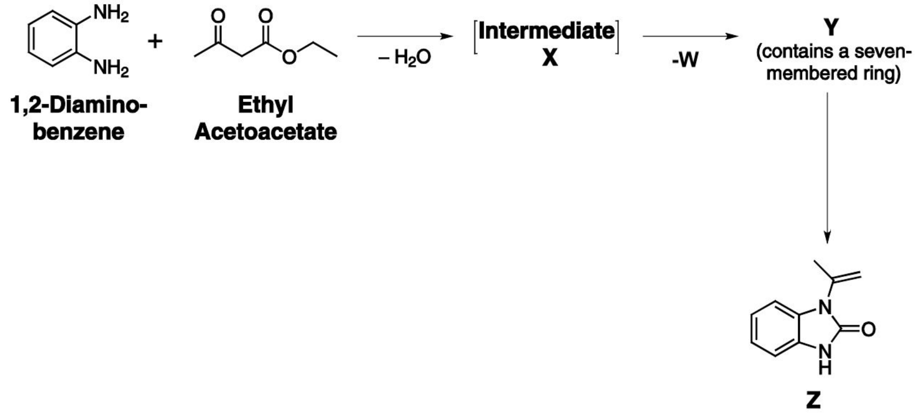


(a) Draw the structures of **A** - **H**

A	**B**	**C**
D	**E**	**F**

G	**H**	

Compound Z itself is synthesized from 1,2-diaminobenzene and ethyl acetoacetate. The synthesis is shown in the scheme below, where all reactions are balanced.



(b) Determine the formula of **W** and draw the structures of Intermediate **X** and Compound **Y**.

W	
X	**Y**

Problem 5
Determination of Calcium Ion 16% of the total

5a	5b	5c	5d	5e	Total	%
2	3	6	8	8	27	16

The calcium content of an aqueous sample can be determined by the following procedure:

Step 1 A few drops of methyl red are added to the acidified aqueous sample, followed by thorough mixing with $Na_2C_2O_4$ solution.

Step 2 Urea ($(NH_2)_2CO$) is added and the solution gently boil until the indicator turns yellow (this typically takes 15 min). CaC_2O_4 precipitates out.

Step 3 The hot solution is filtered and the solid CaC_2O_4 is washed with ice-cold water to remove excess $C_2O_4^{2-}$ ions

Step 4 The insoluble CaC_2O_4 is dissolved in hot 0.1 M H_2SO_4 to give Ca^{2+} ions and $H_2C_2O_4$. The dissolved $H_2C_2O_4$ is titrated with standardized $KMnO_4$ solution until the purple end point is observed.

Relevant reactions and equilibrium constants:

$CaC_2O_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)}$ $K_{sp1} = 1.30 \times 10^{-8}$

$Ca(OH)_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$ $K_{sp2} = 6.50 \times 10^{-6}$

$H_2C_2O_{4\,(aq)} \rightleftharpoons HC_2O_4{}^-{}_{(aq)} + H^+_{(aq)}$ $K_{a1} = 5.60 \times 10^{-2}$

$HC_2O_4{}^-{}_{(aq)} \rightleftharpoons C_2O_4{}^{2-}{}_{(aq)} + H^+_{(aq)}$ $K_{a2} = 5.42 \times 10^{-5}$

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ $K_w = 1.00 \times 10^{-14}$

(a) Write a balanced equation for the reaction that takes place upon the addition of urea (2).

(b) The calcium content of a 25.00 mL aqueous sample was determined using the above procedure and found to require 27.41 mL of a 2.50×10^{-3} M $KMnO_4$ solution in the final step. Find the concentration of Ca^{2+} ions in the sample.

(c) Calculate the solubility of CaC_2O_4 in an aqueous solution buffered at pH 4.0.

In the above analysis, a possible source of error was neglected. The precipitation of CaC_2O_4 in Step 1 will be incomplete if an excess of $C_2O_4^{2-}$ ions is added, due to the following reactions:

$$Ca^{2+}_{(aq)} + C_2O_4{}^{2-}_{(aq)} \rightleftharpoons CaC_2O_{4(aq)} \qquad K_{f1} = 1.0 \times 10^3$$

$$CaC_2O_{4(aq)} + C_2O_4{}^{2-}_{(aq)} \rightleftharpoons Ca(C_2O_4)^{2-}_{(aq)} \qquad K_{f2} = 10$$

(d) Calculate the equilibrium concentrations of Ca^{2+} and $C_2O_4^{2-}$ ions in solution after optimal precipitation of CaC_2O_4 is reached.

(e) Calculate the concentrations of H^+ and Ca^{2+} in a saturated solution of CaC_2O_4. (Neglect activity coefficients. Any assumptions made during calculation must be clearly stated.)

Problem 6
Hydrates of Copper Sulfate **16% of the total**

5a	5b	5c	5d	5e	Total	%
1	3	9	5	4	22	16

Copper(II) Sulfate forms a series of hydrates $CuSO_4 \cdot nH_2O$, where n = 5, 3, 2, 1 and an anhydrous form (n = 0). The hydrates are blue, while the anhydrous salt is colorless and is sometimes used to assess air humidity, e.g. in desiccators (glass vessels for storing samples sensitive to the presence of water vapor). The equilibrium between copper (II) sulfate hydrates and a gas phase containing water vapor can be described by the reaction equations:

(a) $CuSO_4{\cdot}5H_2O_{(s)} \rightleftharpoons CuSO_4{\cdot}3H_2O_{(s)} + 2H_2O_{(g)}$

(b) $CuSO_4{\cdot}3H_2O_{(s)} \rightleftharpoons CuSO_4{\cdot}2H_2O_{(s)} + H_2O_{(g)}$

(c) $CuSO_4{\cdot}2H_2O_{(s)} \rightleftharpoons CuSO_4{\cdot}H_2O_{(s)} + H_2O_{(g)}$

(d) $CuSO_4{\cdot}H_2O_{(s)} \rightleftharpoons CuSO_{4\,(s)} + H_2O_{(g)}$

1.28 g of $CuSO_4 \cdot 5H_2O$ was introduced to an empty cylindrical steel reactor with base radius r = 5.00 cm equipped with a piston to adjust the volume, and the position of the piston was adjusted to make the volume of the reactor V = 1.00 dm^3. The system was then brought to equilibrium at a constant temperature T_1= 400K.

Species	ΔH°_f (298 K) [kJ/mol]	S˚ (298 K) [J/mol /K]	C_p° (298-400 K) [J/mol / K]
$CuSO_4{\cdot}2H_2O$	-1411.2	130.85	171.2
$CuSO_4{\cdot}H_2O$	-1085.1	149.80	131.0
H_2O	-241.80	188.80	28.44

The above table presents selected thermodynamic data for some of the intermediates (C_p° is the average specific constant pressure heat capacity over the indicated temperature range)

In addition, there are functions describing the equilibrium vapor pressure $p_{a/b}$ (in Pa) for conversion between hydrates a and b as a function of the equilibrium temperature (in K)

a) $\text{Log}(p_{5/3})$ = 13.0864-2998.91/T

b) $\text{Log}(p_{3/2})$ = 11.9383-2693.86/T

d) $\text{Log}(p_{1/0})$ = 10.1759-2698.81/T

Gases should be treated as ideal. and assume that when the pressure changes, the new equilibrium is immediately reached. In the calculations, omit the volume of the solid phase

(a) Write the equilibrium constant expressions $K_{a\text{-}d}$ for the reactions studied.

(b) For constant temperature T_1, calculate the vapor pressure values at equilibrium for reactions a, b, and d.

(c) Calculate the final reactor pressure and the number of moles of each individual copper species at steady state at T_1.

(d) The system in equilibrium at T_1 temperature was heated to T_2 = 600 K. Calculate the reactor pressure and the number of moles of individual reactants at temperature T_2.

(e) Calculate how many cm the position of the piston should be changed at temperature T_2, so that the monohydrate appears in the system.

Problem 7
Ligand Chemistry 10% of the total

7a	7b	7c	7d	7e	7f	7g	7h	Total	%
4	2	1	2	5	2	1	4	21	10

Ligand **L** can form complexes with many transition metals. **L** is synthesized by heating a mixture of a bipyridine, glacial acetic acid and hydrogen peroxide to 70 – 80 °C for 3 hrs. The final product **L** crystallizes out as fine needles and its molecular mass is 188.

(a) Determine the molecular formula of **L**.

(b) If **L** is a bidentate chelating ligand, draw the structure of the bipyridine used. Also draw the structure of **L**.

Bipy	**L**

(c) Does the ligand L have any charge, i. e. net charge?

[ ] Yes [ ] No

(d) Draw the structure when one molecule of **L** binds to metal ion (M).

Certain complexes of **L** with Fe and Cr have the formulae of Fe**L**$_m$(ClO$_4$)$_n$·3 H$_2$O (**A**) and Cr**L**$_x$Cl$_y$(ClO$_4$)$_z$·H$_2$O (**B**), respectively. Analysis data of **A** and **B** is given below.

Complex	**Magnetic Moment μ B.M.**	**Elemental analysis (wt %)**	**Color**
A	6.13	Fe 5.740, C 37.030, H 3.090, Cl 10.940, N 8.640	Yellow
B	n/a	Cr 8.440, C 38.930, H 2.920, Cl 17.250, N 9.080	Purple

(e) From the given data determine the empirical formula of **A**. What are the values of m and n in FeL$_m$(ClO4)$_n$·3H$_2$O?

(f) Draw the d-orbital splitting diagram for **A**. Is it high spin or low spin? Justify your answer.

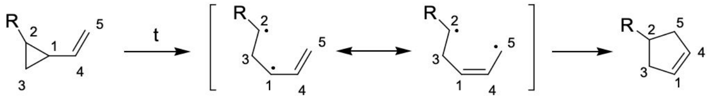
(g) Detail analysis of **B** shows that it contains Cr^{3+} ion. Calculate the spin-only magnetic moment of this compound.

(h) Compound **B** is a 1 : 1 type electrolyte. Determine the empirical formula of **B** and the values of x, y, z in $CrL_xCl_y(ClO4)_z{\cdot}H_2O$.

Problem 8
Vinylcyclopropane rearrangement 14% of the total

8a	8b	8c	Total	%
2	1	24	27	14

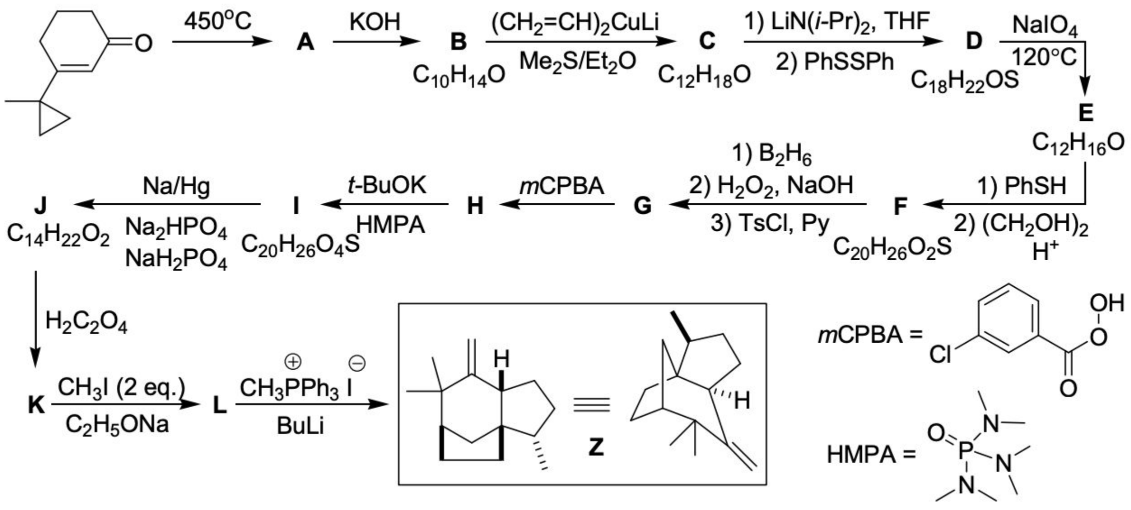
Vinylcyclopropane-to-cyclopentene rearrangement (VCR) as well as the analogous reactions of the corresponding heteroatom compounds are considered the important method for the synthesis of five-membered carbo- and heterocycles. These rearrangements can be performed under thermal, photochemical or catalytic activation. Thermal and photochemical reactions proceed via formation of the most stable biradical.



(a) Write down structural formulae for products of two reactions given below accounting for facts that: a) both reactions are examples of VCR; b) molecule of Y has symmetry axis of the second order.

X	Y

VCR was the first step in the total synthesis of terpene hydrocarbon (±)-zizaene (**Z**):



(b) How many isomers can exist for zizaene?

(c) Draw the structural formulae of compounds **A** – **L**.

A	**B**	**C**
D	**E**	**F**
G	**H**	**I**
J	**K**	**L**

Problem Sources

1	GeCHO 2013 Round 4 #2 Excerpt
2	1996 ICHO #2
3	INCHO 2018 #1
4	UK Oly 2016 #4
5	2005 ICHO Prep #4
6	Polish Olympiad 2017 Stage 3 #3
7	1999 ICHO #4
8	2015 Mendeleev Tour 2 Organic #2

Here are the links to some of the tests which are harder to find (you may need to scroll to find the answer keys)

GeCHO 2013 Round 4 #2 Excerpt
http://wettbewerbe.ipn.uni-kiel.de/icho/aufgaben/archiv/German_Problems_2013.pdf

INCHO 2018 #1
https://olympiads.hbcse.tifr.res.in/olympiads/wp-content/uploads/2017/09/INChO2018-Solution-20180213.pdf

Polish Olympiad 2017 Stage 3 #3
http://www.olchem.edu.pl/63iiit.pdf

2015 Mendeleev Tour 2 Organic #2 (you will need to use webarchive to go back to around June 2018 in order to be able to see the solutions before they were deleted)
http://chem.msu.ru/rus/olimpiad/olimp2015/welcome.html