Code: USA-

Name:

Team Alpha Moo
Mock Camp Test

Theoretical Problems
Exam 3

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

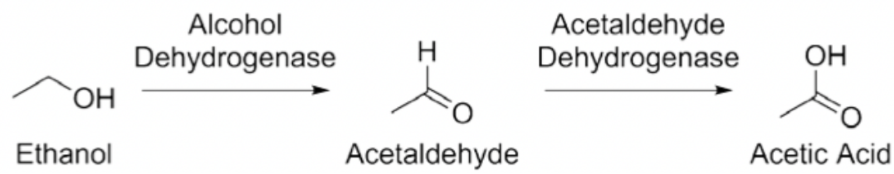
- Write your name only on the cover sheet of the test
- Write your code number on each page (pages with no code will not be graded!)
- You have 2 hours to work on the problems
- Use only the pen and calculator (TI-30XIIS) provided
- All results should be written in the appropriate boxes. If you need 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
CHEMISTRY OF HANGOVERS — 10% of the total

1a	1b	1c	1d	1e	1f	1g	Total	%
0.5	1	2	2	3	0.5	1	10	10

After the consumption of too much alcoholic beverage, people sometimes experience a hangover the following day. There are a variety of causes of a hangover, one of these is the accumulation of the toxic metabolites of ethanol in the body.

In the body, ethanol is first converted into acetaldehyde by the enzyme alcohol dehydrogenase and then into acetic acid by the enzyme acetaldehyde dehydrogenase



In the first step, ethanol reacts with nicotinamide adenine dinucleotide (NAD^+) to form acetaldehyde, a compound called NADH and H^+.

$$\text{Ethanol} + NAD^+ \xrightarrow{\text{Alcohol Dehydrogenase}} \text{Acetaldehyde} + NADH + H^+$$

(a) What happens to the NAD^+ in this reaction?

	It is oxidized
	It is reduced
	It is hydrolyzed
	It is isomerized

In some countries, the legal drink drive limit is 80 mg of ethanol per 100 ml of blood.

(b) What concentration of ethanol does this correspond to (in mol dm^{-3})?

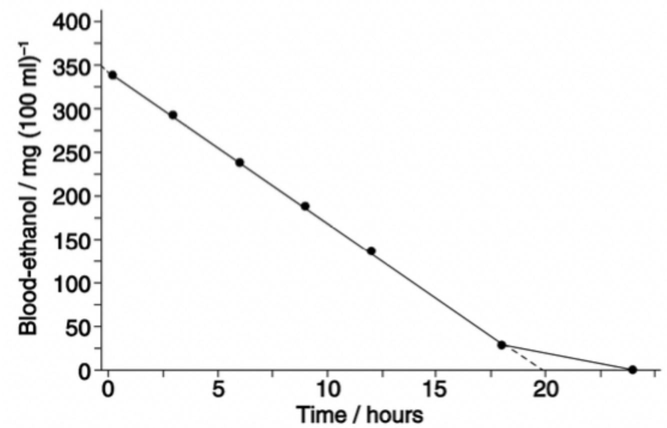
After drinking it is not permitted to drive until the concentration of ethanol has fallen below this level. The reaction to remove ethanol involves the initial combination of the ethanol and the alcohol dehydrogenase to form an enzyme-substrate complex, followed by the conversion of this complex into products. The rate of this reaction (the rate of production of acetaldehyde) has a rate law directly following the Michaelis Menten equation where

- $k_2 = 1.33 s^{-1}$, the rate constant for the conversion of the enzyme substrate complex into products
- $K_m = 1.00 \times 10^{-3}$ mol dm^{-3} = $^{(k-1+k2)}/_{(k1)}$

(c) Write the rate equation for the rate of formation of acetaldehyde

(d) What is the order of this reaction with respect to ethanol around the legal drinking limit from part (b)?

The graph on the right shows how the blood ethanol concentration of someone who has drunk a lot of alcohol varies over time.



(e) What concentration of alcohol dehydrogenase enzyme does this person have?

(f) The half-life of this reaction is the time taken for the concentration of ethanol to fall to half of its initial value. From the graph, how does the half-life vary over the majority of the period this person is sobering up?

	It increases
	It is constant
	It decreases

(g) For a different poisonous alcohol, alcohol dehydrogenase has a $k_2 = 1.10\ s^{-1}$ and a $K_M = 3.2 \times 10^{-2}$ mol dm^{-3}. What can be concluded about the metabolism of this alcohol? Tick all that apply.

	The maximum rate of metabolism is faster for ethanol
	The maximum rate of metabolism is faster for the poisonous alcohol
	The maximum rate of metabolism is the same for both
	A higher concentration of ethanol is needed for the reaction to proceed at half of its maximum rate
	A higher concentration of the poisonous alcohol is needed for the reaction to proceed at half of its maximum rate
	The same concentration of ethanol and the poisonous alcohol are needed for the reactions to proceed at half of their maximum rate
	The metabolism of the poisonous alcohol follows a rate law different from that of ethanol

Problem 2
URANYL EXTRACTION 14% of the total

2a	2b	Total	%
8	6	14	14

Bis(2-ethylhexyl) hydrogen phosphate (di-(2-ethylhexyl)phosphoric acid, DEHPA) is used in the extraction of uranyl ions from an aqueous solution to an organic solvent. This water-to-kerosene extraction is known as the "Dapex process".

DEHPA (HA)

- Is a weak acid that is partially dissociated in water, with a dissociation constant

$$\mathrm{HA} \rightleftharpoons \mathrm{A^-} + \mathrm{H^+} \qquad K_{\mathrm{a,HA}} = \frac{[\mathrm{A^-}]_{\mathrm{aq}} \times [\mathrm{H^+}]_{\mathrm{aq}}}{[\mathrm{HA}]_{\mathrm{aq}}} = 3.16 \times 10^{-4}$$

- Can be extracted to kerosene with a distribution constant

$$K_{\mathrm{D,HA}} = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{HA}]_{\mathrm{aq}}} = 1.89 \times 10^{2}$$

- Forms a hydrogen-bonded dimer in non-polar organic solvents, with a dimerization constant

$$2\mathrm{HA} \rightleftharpoons (\mathrm{HA})_2 \qquad K_{\mathrm{p,HA}} = \frac{[(\mathrm{HA})_2]_{\mathrm{org}}}{[\mathrm{HA}]^2_{\mathrm{org}}} = 2.14 \times 10^{4}$$

- When dissociated in an aqueous solution, it forms a neutral compound with the uranyl ion in a ratio of 2:1 (Note: In real systems, the structure of the neutral compound can vary).

$$2\mathrm{A^-} + \mathrm{UO_2^{2+}} \rightleftharpoons \mathrm{UO_2A_2} \qquad \beta_{2,\mathrm{UO_2A_2}} = \frac{[\mathrm{UO_2A_2}]_{\mathrm{aq}}}{[\mathrm{A^-}]^2_{\mathrm{aq}} \times [\mathrm{UO_2^{2+}}]_{\mathrm{aq}}} = 4.31 \times 10^{11}$$

  This neutral compound can be extracted to kerosene with a distribution constant

$$K_{\mathrm{D,UO_2A_2}} = \frac{[\mathrm{UO_2A_2}]_{\mathrm{org}}}{[\mathrm{UO_2A_2}]_{\mathrm{aq}}} = 1.69 \times 10^{2}$$

Assume that:

- The concentration of DEHPA before the extraction: $c_{\mathrm{HA,org,0}}$ = 0.500 mol dm^{-3} and $c_{\mathrm{HA,aq,0}}$ = 0.000 mol dm^{-3}.
- $c_{\mathrm{UO_2^{2+}}} \ll c_{\mathrm{HA}}$, therefore it is possible to omit the concentration of UO_2A_2 in the mass balance of HA in both the aqueous and organic phase.
- The volume ratio is $V_{\mathrm{org}}/V_{\mathrm{aq}}$ = 1.00.

Uranyl ions also form hydroxo complexes

$$UO_2^{2+} + iOH^- \rightleftharpoons [UO_2(OH)_i]^{2-i} \quad \text{where } i = 1\text{–}4$$

$$\beta_{i,[UO_2(OH)_i]} = \frac{[UO_2(OH)_i^{2-i}]_{aq}}{[UO_2^{2+}]_{aq} \times [OH^-]_{aq}^i}$$

Note: For clarity square brackets as a symbol for a complex were omitted in the numerator.

with decimal logarithms of the overall complexation constants log β_1 = 10.5, log β_2 = 21.2, log β_3 = 28.1, log β_4 = 31.5.

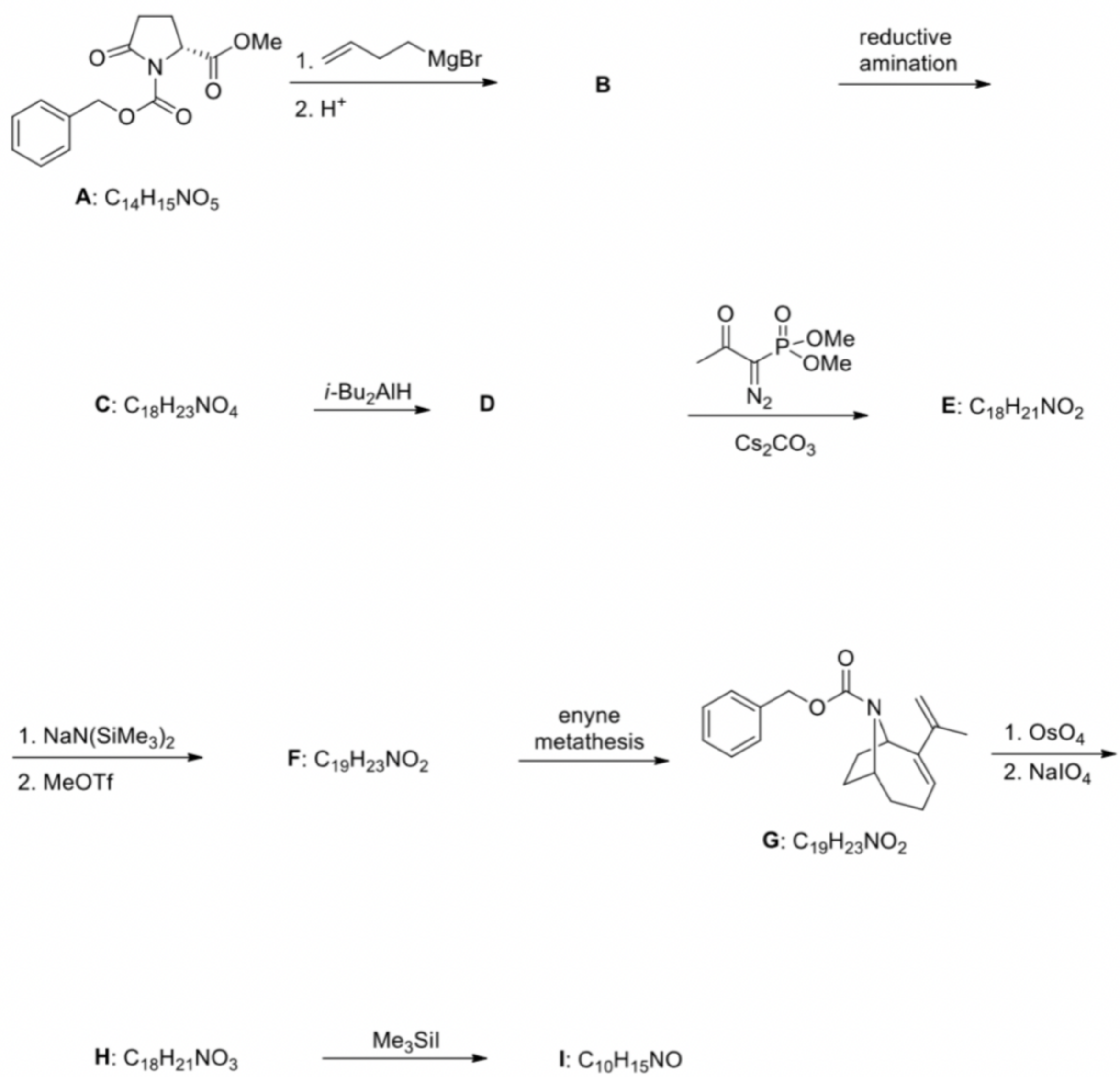
(a) Considering that the pH of the aqueous phase after reaching equilibrium equals to 1.7, calculate the yield of uranyl ions extraction.

(b) Considering that the pH of the aqueous phase after reaching equilibrium equals to 10.3, calculate the yield of uranyl ions extraction.

Problem 3
SYNTHESIS OF ANATOXIN-A & ILLUDIN-C — 14% of the total

3a	3b	Total	%
10	8	18	14

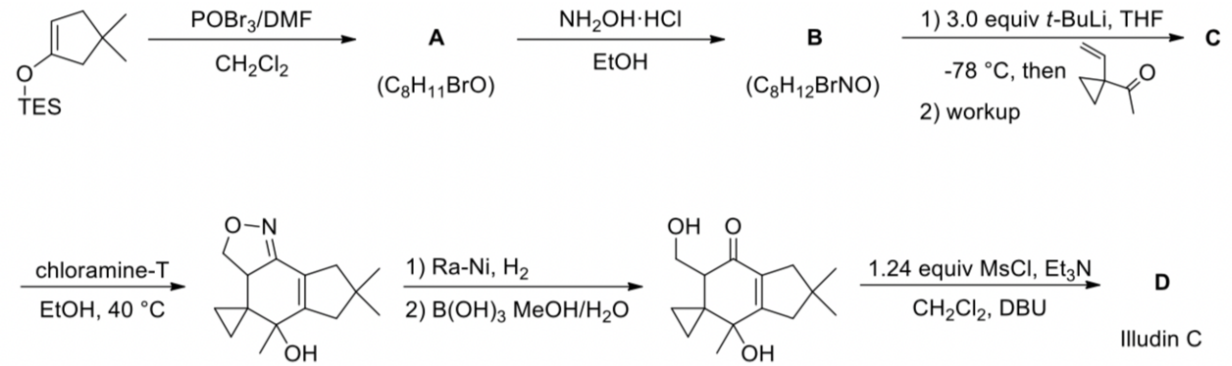
Anatoxin-a (**I**) is a secondary amine alkaloid with acute neurotoxicity that can cause death by respiratory paralysis. This compound is produced by several different genera of cyanobacteria found all over the world. In 2004, Jehrod B. Brenneman and Stephen F. Martin reported a concise synthesis of anatoxin-a from commercially available D-methyl pyroglutamate, which was converted to compound **A**.



(a) Write down the structural formulae of compounds **B**-**F**, **H** and **I** in the boxes provided.

<table>
<tr><td>B</td><td colspan="2">C</td><td>D</td></tr>
<tr><td colspan="2">E</td><td colspan="2">F</td></tr>
<tr><td colspan="2">H</td><td colspan="2">I</td></tr>
</table>

During the synthesis of sesquiterpene (±)-illudin C, R. L. Funk required the building block **C** which could be prepared based on the short synthesis shown below. Compound **C** was then carried on in the synthesis as shown. Provide the correct structures of **A**, **B**, **C** and **D**.



(b) Write down the structural formulae of compounds **A**, **B**, **C** and **D** in the boxes provided.

A	**B**
C	**D**

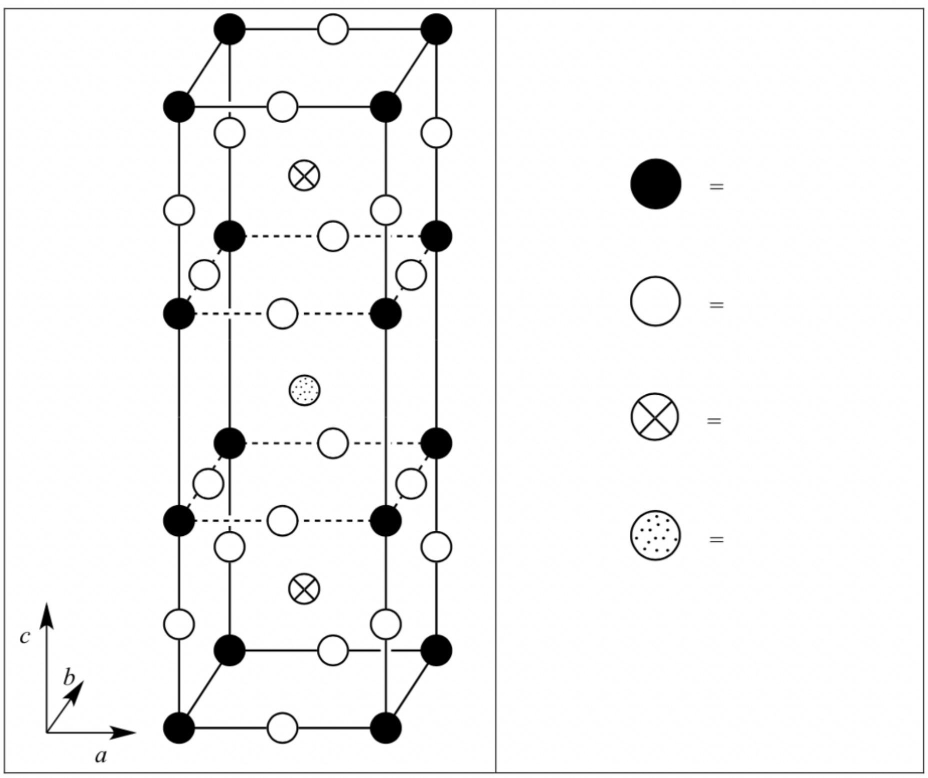
Problem 4
ANALYSIS OF YBCO

15% of the total

4a	4b	4c	4d				4e		Total	%
2	4	2	i	ii	iii	iv	i	ii	15	15
			1	1	1	1	2	3		

In the 1980's a class of ceramic materials was discovered that exhibits superconductivity at the unusually high temperature of 90 K. One such material contains yttrium, barium, copper and oxygen and is called "YBCO". It has a nominal composition of $YBa_2Cu_3O_7$, but its actual composition is variable according to the formula $YBa_2Cu_3O_{7-\delta}$ ($0 < \delta < 0.5$).

(a) One unit cell of the idealized crystal structure of YBCO is shown below. Identify which circles correspond to which elements in the structure.



The true structure is actually orthorhombic *(a ≠ b ≠c),* but it is approximately tetragonal, with a>> b >> (c/3)

(b) A sample of YBCO with $\delta = 0.25$ was subjected to X-ray diffraction using CuKα X-rays (λ = 154.2 pm). The lowest-angle diffraction peak was observed at $2\theta = 7.450°$. Assuming that *a = b = (c/3)*, calculate the values of a and c.

(c) Estimate the density of this sample of YBCO (with $\delta = 0.25$) in g cm^{-3}. If you do not have the values for a and c from part (b), then use a = 500. pm, c = 1500. pm.

(d) When YBCO is dissolved in 1.0 M aqueous HCl, bubbles of gas are observed (identified as O_2 by gas chromatography). After boiling for 10 min to expel the dissolved gases, the solution reacts with excess KI solution, turning yellow-brown. This solution can be titrated with thiosulfate solution to a starch endpoint. If YBCO is added directly to a solution that 1.0 M in both KI and HCl under Ar, the solution turns yellow-brown but no gas evolution is observed.

(i) Write a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl with evolution of O_2.

(ii) Write a balanced net ionic equation for the reaction when the solution from (i) reacts with excess KI in acidic solution after the dissolved oxygen is expelled.

(iii) Write a balanced net ionic equation for the reaction when the solution from (ii) is titrated with thiosulfate ($S_2O_3^{2-}$).

(iv) Write a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl containing excess KI in an Ar atmosphere.

e) Two identical samples of YBCO with an unknown value of d were prepared. The first sample was dissolved in 5 mL of 1.0 M aqueous HCl, evolving O_2. After boiling to expel gases, cooling, and addition of 10 mL of 0.7 M KI solution under Ar, titration with thiosulfate to the starch endpoint required $1.542 \cdot 10^{-4}$ mol thiosulfate. The second sample of YBCO was added directly to 7 mL of a solution that was 1.0 M in KI and 0.7 M in HCl under Ar; titration of this solution required $1.696 \cdot 10^{-4}$ mol thiosulfate to reach the endpoint.

(i) Calculate the number of moles of Cu in each of these samples of YBCO.

ii) Calculate the value of δ for these samples of YBCO.

Problem 5
HALOGEN CHEMISTRY 13% of the total

5a			5b	5c	5d	5e	5f	5g	5h	5i	5j	Total	%
i	ii	ii	3	1	2	1	1	2	3	2	2	19	13
1	1	2											

Halogens in their reactions among themselves and with a variety of other elements give rise to a large number of compounds with diverse structure, bonding and chemical behaviour. Metal halides, halogen derivatives and interhalogens represent major types of halogen compounds.

(a) A "black and white" photographic film contains a coating of silver bromide on a support such as cellulose acetate.

(i) Write the photochemical reaction that occurs when light falls on AgBr(s) coated on a film.

(ii) During the developing process, unexposed AgBr is washed away by complexation of Ag(I) by sodium thiosulphate solution. Write down this chemical reaction.

(iii) These washings are often disposed of as waste. However, metallic silver can be recovered from them by adding cyanide, followed by zinc. Write down the reactions involved.

Fluorine, can react with other halogens Cl_2, Br_2 and I_2 under controlled conditions.
A mixture of iodine vapour and chlorine gas when fed into a mass spectrometer gave two sets (A and B) of mass spectral peaks corresponding to molecular ions of two chemical species at m/z:
A: 162, 164
B: 464, 466, 468, 470, 472, 474, 476

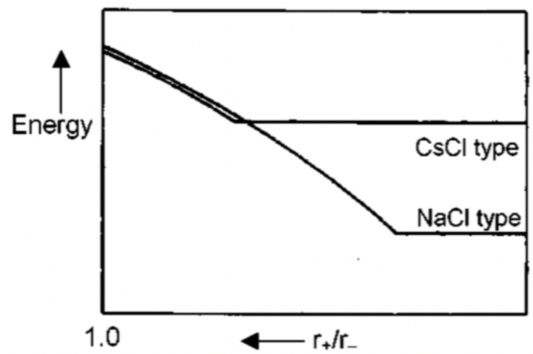
(b) Identify the molecular species corresponding to m/z = 162, 164, 466 and 476. Draw the structure of the heaviest species (m/z = 476) indicating clearly the lone pairs on atom(s) of I (iodine). Show the isotopic composition of each species.

162	164	466	476

(c) In aqueous medium chlorine gas oxidises sodium thiosulphate. Write down the chemical equation for this reaction.

(d) Chlorine dioxide reacts with sodium hydroxide forming two products **X** and **Y** containing chlorine. Identify the products X and Y (both containing chlorine) and balance the equation.

X-ray crystallography reveals many aspects of the structure of metal halides. The radius ratio (r+/r–) is a useful parameter to rationalise their structure and stability. A table of radius ratio (r+/r–) for some alkali halides with radius ratio (r– kept constant) is shown schematically for NaCl-type and CsCl-type crystal structures.



	Li^+	Na^+	K^+	Rb^+	Cs^+
Cl^-	0.33	0.52	0.74	0.82	0.93
Br^-	0.31	0.49	0.68	0.76	0.87
I^-	0.28	0.44	0.62	0.69	0.78

(e) For a given anion, the graph for NaCl-type structure levels off at low r+/r– values because of

	cation-cation contact along the face diagonal.
	anion-anion contact along the face diagonal.
	cation-anion contact along the cell edge.

(f) Which among the halides LiBr, NaBr and RbBr is likely to undergo phase transition from NaCl-type to CsCl-type structure with change of temperature and / or pressure?

(g) Show by calculation the radius ratio (r+/r–) at which the energy of CsCl-type structure levels off.

Using CuKα X-rays (λ = 154 pm), diffraction by a KCl crystal (fcc structure) is observed at an angle (θ) of 14.2 °.

- Diffraction takes place from the planes with $h^2+k^2+l^2 = 4$
- In a cubic crystal $d_{hkl}=a/(h^2+k^2+l^2)^{1/2}$, where "d" is the distance between adjacent hkl planes and "a" is a lattice parameter
- Reflections in a FCC structure can occur only from planes with all odd or all even hkl indices

(h) calculate the lattice parameter "a" for KCl.

(i) Indicate in the table given below the required information for the 2nd and 3rd nearest neighbors of a K^+ ion in the KCl lattice.

2nd nearest neighbours			3rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)

(j) Determine the lowest value of diffraction angle θ possible for the KCl structure.

Problem 6
THE TIN PEST   12% of the total

6a	6b	Total	%
2	10	12	12

The ductility and malleability typical of metals has made metals essential structural elements in modern construction. The thermodynamically stable form of elemental tin at 298 K and ambient pressure is white tin (density = 7.29 g cm^{-3}), which has mechanical properties typical of metals and therefore can be used as a building material. At lower temperatures, however, a second allotrope of tin, gray tin (density = 5.766 g cm^{-3}), becomes thermodynamically stable. Because gray tin is much more brittle than white tin, structural elements made of tin that are kept at low temperatures for prolonged periods may crumble and fail. Because this failure resembles a disease, it has been termed the "tin pest".

(a) Given the thermodynamic data below, calculate the temperature at which gray Sn is in equilibrium with white Sn (at 1 bar = 10^5 Pa pressure).

Substance	$\Delta H_f°$ (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
Sn (s, gray)	-2.016	44.14
Sn (s, white)	0.000	51.18

(b) The pressure at the bottom of the Mariana Trench in the Pacific Ocean is 1090 bar. Will the temperature at which the two allotropes of tin are in equilibrium increase or decrease at that pressure, and by how much? In your quantitative calculations, you may assume that the internal energy (U), entropy (S), and molar volume of the two phases of tin are independent of temperature and pressure.

Problem 7
ELECTRONS IN A RING 10% of the total

7a	7b	7c	7d	Total	%
3	2	1	4	10	10

For description of the π electronic states of a benzene molecule, it is possible to apply a model involving free electrons moving in a circle of radius *r*. In this model the electronic energy levels are described as follows.

$$E_n = \frac{n^2 \hbar^2}{2mR^2}$$

- $\hbar$ = 1.05 x 10^{-34} J s = $h/2\pi$
- m_e = 9.11 x 10^{-31} kg
- n = quantum number (n=…-2, -1, 0, 1, 2 …)

a) Draw the distribution of π electrons over the energy levels of the benzene molecule according to the proposed model. What is the quantum number *n* corresponding to the highest occupied electron level of C_6H_6? How many unpaired electrons does Benzene have according to this model?

(b) Calculate the radius of the π electron's motion in the C_6H_6 molecule taking into account that the energy difference between the highest occupied and lowest unoccupied levels is equal to 600 kJ/mol.

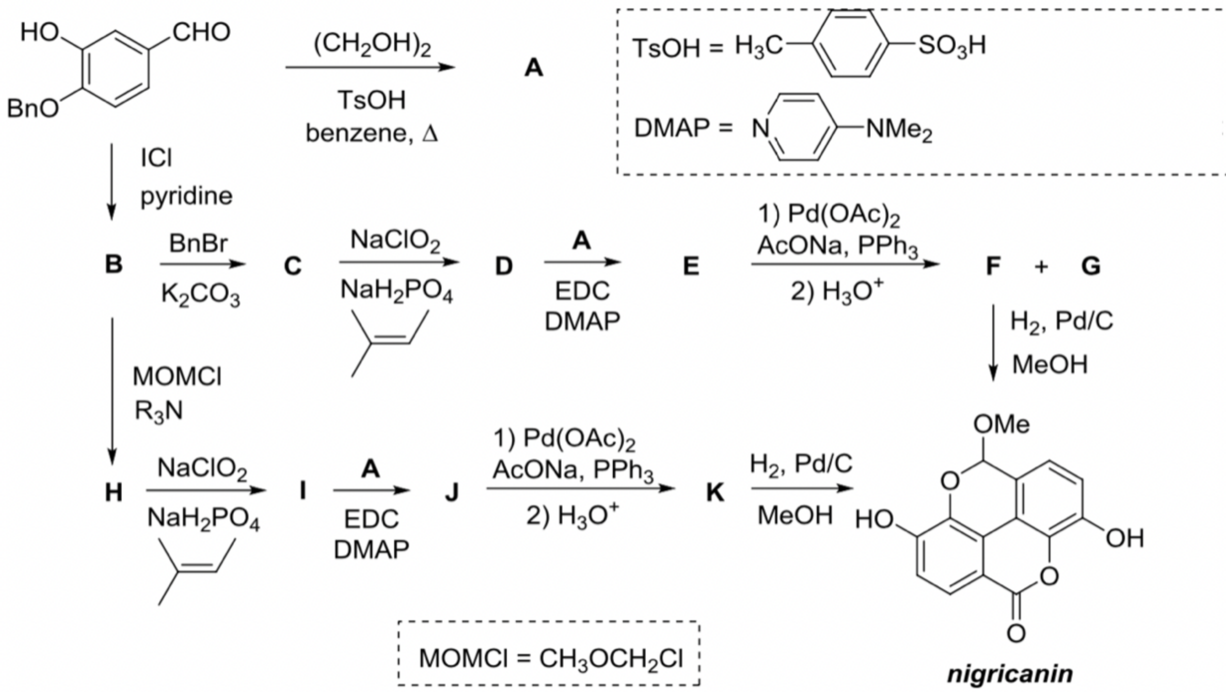
(c) What is the Carbon-Carbon bond length in benzene under the assumption that the sigma-skeleton is inscribed into the circle along which the electrons are moving.

(d) [14] Annulene ($C_{14}H_{14}$) is a cyclic compound with a conjugated bond system having a planar structure. Using the C-C bond length from (c), determine the energy difference in kJ/mol of the highest occupied and lowest unoccupied energy levels of [14] Annulene. Assume that the circle circumference is equal to the sum of the C-C bond lengths.

Problem 8
TWO IN ONE — 12% of the total

8a	Total	%
22	22	12

Ellagic acid and its family exhibit antioxidant, anti-cancer, and other types of biological activity. Very recently, the first total synthesis of nigricanin, one of the ellagic acid congeners, was described. **F** and **G** are isomers; molecular formulae of **D** and **E** are $C_{21}H_{17}IO_4$ and $C_{37}H_{31}IO_7$, respectively.



(a) Draw the structural formulae of compounds **A**–**K**

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

If you would like to grade this, you should look up the answer keys in each respective test from which the problems were taken. These can be easily found online.

Problem Sources

1	2015 UK Olympiad #4
2	2018 ICHO Prep #12
3	2017 ICHO Prep #29 & 30
4	2012 ICHO #4
5	2001 ICHO #5
6	2012 ICHO Prep #5
7	2003 Mendeleev Tour 2 PChem #1
8	2015 ICHO Prep #19