Chinese Chemistry Olympiad

2012

3 Hours

Question	1	2	3	4	5	6	7	8	9	10	11	Total
Points	7	7	10	5	8	7	10	16	12	6	12	100

PERIODIC TABLE OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Problem 1 [7%]

1-1 Aqueous ammonia of appropriate concentration is added dropwise to the aqueous solution of zinc sulfate to an excess, and two main reactions occur. Briefly describe the experimental phenomena and write the ion equation for the two-step main reaction.

The solution will first exhibit a white gelatinous precipitate of $Zn(OH)_2$ followed by redissolution due to complexation to form $Zn(NH_3)_4^{2+}$

1) $Zn^{2+} + 2NH_3 + 2H_2O \rightarrow Zn(OH)_2(s) + 2NH_4^+$
2) $Zn(OH)_2 + 2NH_4^+ + 2NH_3 \rightarrow [Zn(NH_3)_4^{2+}](aq) + 2H_2O$

1-2 The compound $[Cu(pydc)(amp)]\cdot 3H_2O$ has formula $C_{11}H_{14}CuN_4O_7$ (pydc and amp are organic ligands containing aromatic rings). Thermogravimetric analysis shows that the compound thermally decomposes in two steps. The first weight loss peak accounts for a weight loss of approximately 15%. The second decomposition occurs between 400 and 500 ºC leaving behind a solid residue with a mass of 21% of the original compound mass. Determine the following:

Relevant Paper:
https://www.researchgate.net/publication/221765752_Supramolecular_assembled_of_hexameric_water_clusters_into_a_1D_chain_containing_H2O6_and_H2O4O2_stabilized_by_hydrogen_bonding_in_a_copper_complex

(1) What causes the weight loss occurring during the first step?

The answer is likely loss of H_2O. $MW(C_{11}H_{14}CuN_4O_7) = 377.55$ g/mol.

$0.15\cdot 377.55 = 56.63$ which is in the realm of experimental error for $3\cdot 18 = 54$ g/mol

Indeed, $3\cdot 18/377.55 = 14.3\% \approx 15\%$

(2) What is the solid residue remaining after further heating to 500ºC? Justify your answer.

$377.55\cdot 0.21 = 79.29$ g/mol which is close to MW(CuO) = 79.55 g/mol (within experimental error)

Thus the solid residue is CuO. Note that the original question listed a mass % of 20.0 which was the actual figure reported in the paper. This leads to a molar mass of 75.51 g/mol. As a result the official answer says something like a mixture of CuO and Cu_2O, but at high temperature equilibrium I find this answer unlikely, so I modified the numbers.

Problem 2 [7%]

A and **X** are two common non-metallic elements. The sum of their atomic numbers is 22, and the sum of their valence layer electron counts is 10. Under certain conditions, **AX**, AX_3 (a common Lewis acid), A_2X_4 and A_4X_4 can be generated.

$$A(s) + 3/2\ X_2(g) \rightarrow AX_3(g)$$

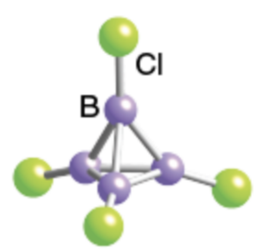
After being passed through a mercury electrical discharge, the following reactions can follow

$$AX_3(g) \rightarrow AX(g) + 2X(g)$$
$$2Hg + 2X(g) \rightarrow Hg_2X_2(g)$$
$$AX(g) + AX_3(g) \rightarrow A_2X_4(g)$$
$$4AX(g) \rightarrow A_4X_4(s)$$

2-1 Determine the identities of **A** and **X**

A:B	**X:Cl**

2-2 A_4X_4 has 4 three-fold rotation axes, and there are 4 atoms around each **A** atom. Draw the structural formula of A_4X_4



2-3 Write the equation for the reaction of AX_3 with CH_3MgBr in a 1:3 molar ratio.

All acceptable:
$BCl_3 + 3CH_3MgBr \rightarrow B(CH_3)_3 + 3\ MgBrCl$
$AX_3 + 3CH_3MgBr \rightarrow A(CH_3)_3 + 3\ MgBrX$
$BCl_3 + 3CH_3MgBr \rightarrow B(CH_3)_3 + 3/2\ MgBr_2 + 3/2\ MgCl_2$

2-4 Write the equation for the alcoholysis of A_2X_4 by ethanol.

All acceptable:
$B_2Cl_4 + 4\ C_2H_5OH \rightarrow B_2(OC_2H_5)_4 + 4HCl$
$A_2X_4 + 4\ C_2H_5OH \rightarrow A_2(OC_2H_5)_4 + 4HX$

Problem 3 [10%]

Aqueous solutions of $CuSO_4$ can react with $K_2C_2O_4$ to form a blue crystal of unknown composition. The formula of the crystal was determined by the following experiments

(a) Weigh 0.2073 g of the sample, put it into an Erlenmeyer flask, add 40 mL of 2 mol L^{-1} H_2SO_4, and dissolve the sample with slight heat. Add 30 mL of water, heat to near boiling, titrate with 0.02054 mol L^{-1} $KMnO_4$ solution to the end. This step requires 24.18 mL of titrant.

(b) Next, the solution is sufficiently heated until the color changes from lavender to blue. After cooling, 2g of KI solid and an appropriate amount of Na_2CO_3 were added. The solution turned brown and a precipitate was formed. The solution was titrated with 0.04826 mol L^{-1} $Na_2S_2O_3$ solution, with starch indicator added near the end point, to the end point, consuming 12.69 mL.

3-1 Write the equation for the titration reaction occurring in step (a).

$2MnO_4^- + 4\ H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10\ CO_2\ (g) + 8H_2O$ *

3-2 Write the equation for the reaction causing the color change from lavender to blue in step (b).

$4MnO_4^- + 12H^+ \rightarrow Mn^{2+} + 5O_2\ (g) + 6H_2O$

3-3 Write the reaction occurring upon addition of KI in step (b). Also write the equation for the $Na_2S_2O_3$ titration reaction.

KI reacts with Cu^{2+} to form a white precipitate of CuI and a brown solution of I_3^-

$2Cu^{2+} + 5\ I^- \rightarrow 2CuI\ (s) + I_3^-$

3-4 Determine the chemical formula of the blue crystal by calculation (all coefficients in the formula are integers)

$n(C_2O_4^{2-}) = 0.02054\ M\cdot 24.18\ ml\cdot 5/2 = 1.241\ mmol$

$n(Cu^{2+}) = 0.04826\ M\cdot 12.69\ ml = 0.6124\ mmol$

$n(C_2O_4^{2-}) \approx 2\ n(Cu^{2+}) \rightarrow$ Solid contains $[Cu(C_2O_4)_2^{2-}]$

Between Cu^{2+} and K^+ for the counterion, K^+ is more likely (although you can test both).

So the crystal has the formula $K_2Cu(C_2O_4)\cdot xH_2O$

If we try using the formula:

$$n(H_2O) \cdot 18\ g/mol = 0.2073 - n(Cu^{2+})\cdot MW(K_2Cu(C_2O_4)_2)$$

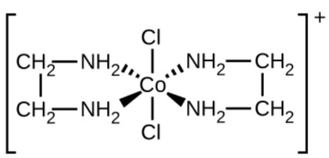
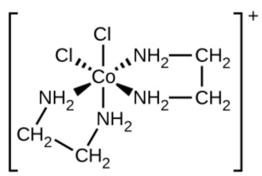
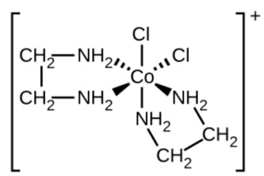
$$n(H_2O) \cdot 18\ g/mol = 0.2073 - 0.5\cdot n(C_2O_4^{2-})\cdot MW(K_2Cu(C_2O_4)_2)$$

We get $x = n(H_2O)/n(Cu^{2+}) = 1.15$ and 0.989 respectively, which tells us that the complex is a monohydrate.

$\mathbf{K_2Cu(C_2O_4)_2\cdot H_2O}$

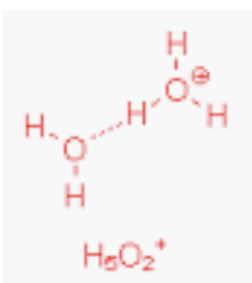
Problem 4 [5%]
Neutron diffraction experiments carried out in 1967 determined that there are only three ions in the crystal structure of trans-$[Co(en)_2Cl_2]Cl{\cdot}HCl{\cdot}2H_2O$: **X**$^+$, Cobalt-containing **A**$^+$ and Cl^-. All atoms in **X**$^+$ are coplanar. **X**$^+$ also has a center of symmetry and three mirror planes that are perpendicular to each other. Note: en is an abbreviation for ethylenediamine.
Relevant Paper:
https://www.sciencedirect.com/science/article/abs/pii/0020165067800862?via%3Dihub

4-1 Draw the structural formula of the stereoisomers of **A**$^+$ and its stereoisomers

A$^+$:	Stereoisomers
trans form 	*cis* form (optical isomers)  

4-2 Draw the structural formula of **X**$^+$.

X$^+$ = $H_5O_2^+$ (very technically this is not planar, but oh well)



Problem 5 [8%]
A supramolecular crystal is obtained by mixing aqueous solutions of urea and oxalic acid. X-ray diffraction experiments showed that the crystal belongs to the monoclinic system, with unit cell parameters a = 505.8 pm, b = 1240 pm, c = 696.4 pm, β = 98.13°. The crystal's supramolecular structure is caused by hydrogen bonding between adjacent molecules leading to a two-dimensional lattice. The crystal has density D = 1.614 g·cm^{-3}.

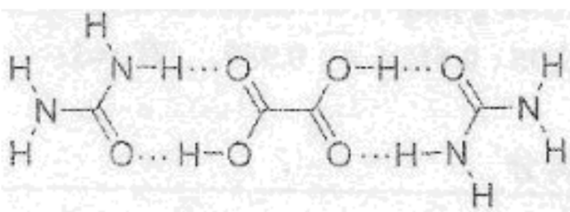
5-1 Determine the ratio of oxalic acid molecules to urea molecules present in the crystal.

V = *abc* sin(*β*) = 4.32·10^{8}pm
D = MW(formula unit)/V → MW(formula unit) = 420.25 g.mol

MW($H_2C_2O_4$) = 90 g/mol, MW($OC(NH_2)_2$) = 60 g/mol
From guess and check we get 4·60 + 2·90 = 420 g/mol

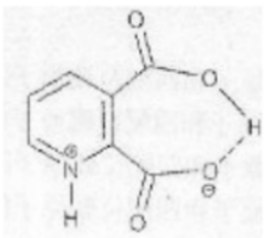
Thus the ratio of oxalic acid molecules to urea molecules is 1: 2

5-2 Using structural formulas draw the hydrogen bonding in a formula unit of the crystal

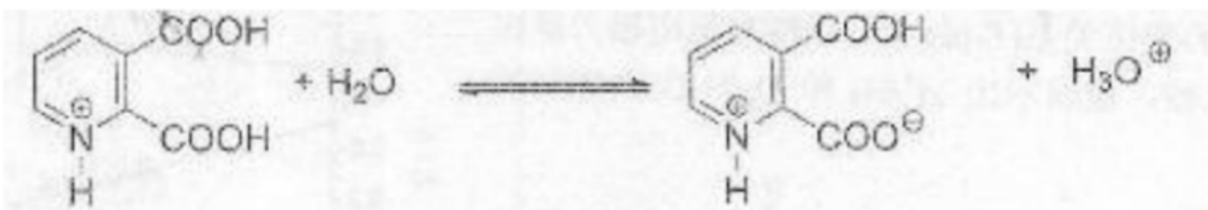


Problem 6 [7%]
2,3-pyridinedicarboxylic acid, commonly known as quinolinic acid, is a central neurotoxin related to Alzheimers and Parkinsons. At room temperature, quinolinic acid exists as a solid, and upon heating at 185-190 ºC, CO_2 is released forming niacin.

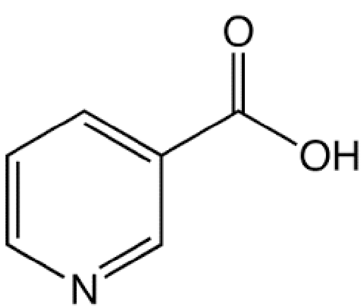
6-1 In the solid state, quinolinic acid adopts its lowest energy configuration. Draw this configuration (you do not need to draw lone pairs or irrelevant hydrogen atoms).



6-2 the pK_{a1} of quinolinic acid in aqueous solution is 2.41, write the equation for its first ionization (draw organic molecules as structural formulas).



6-3 Draw the structure of niacin.

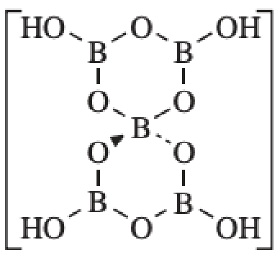


Problem 7 [10%]

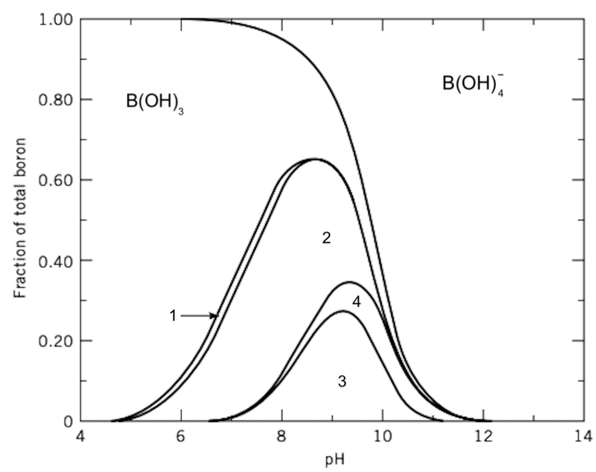
In aqueous solutions of boric acid with a total boron concentration of ≥ 0.4 mol L^{-1}, ions like tetraborate ($B_4O_5(OH)_4^{2-}$), pentaborate (which has charge –1), and two distinct kinds of triborate ions with charges -1 and -2 can form. These polyborate ions are formed by condensation of $B(OH)_3$ and $B(OH)_4^-$. The boron atoms in the structure are connected to form a ring by oxygens in a B-O-B fashion.

Source Paper:
https://onlinelibrary.wiley.com/doi/10.1002/0471238961.0215181519130920.a01.pub2

7-1 In the above pentaborate ions, the chemical environment of all three coordinated boron atoms is exactly the same. Draw the structural formula for pentaborate (you do not need to draw lone pairs)



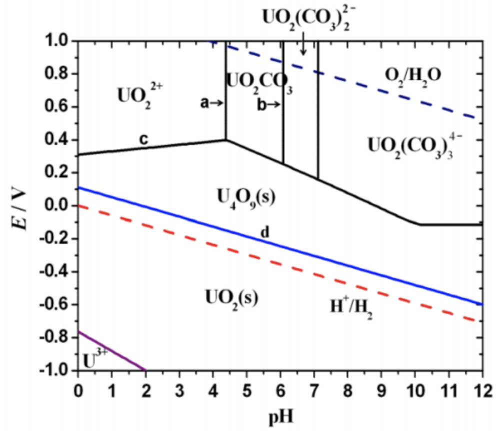
7-2 The figure on the right shows the relationship between the existence form and pH of the boric acid-borate system when the total concentration of boron is 0.4 mol L^{-1}. The numbered areas (labeled 1,2,3,4) between the curves represent the fractional composition of the 4 kinds of polyborate ions at each pH. Determine the chemical formulas of the polyborate ions 1-4.



1: $B_5O_6(OH)_4^-$	2: $B_3O_3(OH)_4^-$
3: $B_4O_5(OH)_4^{2-}$	4: $B_3O_3(OH)_5^{2-}$

Problem 8 [16%]
The pourbaix diagram on the right shows the relationship between the most stable species of uranium over a range of cell potentials and pH in a the carbonic acid-carbonate system (total carbonate concentration 1.0×10^{-2} mol L^{-1}) using the standard hydrogen electrode as the reference value.

For comparison, the dashed lines show the E-pH relationship for H^+/H_2 and O_2/H_2O pairs.



8-1 Calculate the concentrations of the main species in a carbonic acid-carbonate system at pH of 4.0 and 6.0 respectively
H_2CO_3: $K_{a1} = 4.5 \cdot 10^{-7}$, $K_{a2} = 4.7 \cdot 10^{-11}$

Note that this first part has nothing to do with Uranium (it's just about the bicarbonate system)
$C_{tot} = 1.0 \cdot 10^{-2}$ M $= [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$[HCO_3^-] = K_{a1} \cdot [H_2CO_3]/[H^+]$, $[CO_3^{2-}] = K_{a1}K_{a2} [H_2CO_3]/[H^+]^2$
At both pH values H_2CO_3 dominates.

At pH = 4, it is safe to assume **$[H_2CO_3] \approx 1.0 \cdot 10^{-2}$ M**
It follows that **$[HCO_3^-] = 4.5 \cdot 10^{-5}$ M, $[CO_3^{2-}] = 2.115 \cdot 10^{-9}$ M**

At pH = 6, $[HCO_3^-]$ and $[H_2CO_3]$ are the primary species, $[CO_3^{2-}]$ is comparatively negligible.

$[HCO_3^-]/[H_2CO_3] = K_{a1}/[H^+] = 0.45$, so $C_{tot} = 1.45\ [H_2CO_3]$, so **$[H_2CO_3] = 6.90 \cdot 10^{-3}$ M**
It follows that **$[HCO_3^-] = 3.10 \cdot 10^{-3}$ M, $[CO_3^{2-}] = 1.46 \cdot 10^{-7}$ M**

8-2 In the figure, a and b are two straight lines with pH = 4.4 and 6.1, respectively. Write the equations for the transformation of uranium species corresponding to a and b, respectively.

Recall that H_2CO_3 is the primary species at these pH values

a: $UO_2^{2+} + H_2CO_3 \rightarrow UO_2CO_3 + 2H^+$

b: $UO_2CO_3 + H_2CO_3 \rightarrow UO_2(CO_3)_2^{2-} + 2H^+$

8-3 Write the half cell potential equations for the reactions corresponding to the straight lines c and d, respectively, and explain the reason for the positive or negative slope.

The reaction for line c is

$$4UO_2^+ + H_2O + 2e^- \rightarrow U_4O_9 + 2H^+$$

The reaction for line d is

$$U_4O_9 + 2H^+ + 2e^- \rightarrow 4UO_2 + H_2O$$

The equations for the lines comes from the nernst equation for each half reaction. Above this potential, the oxidation is spontaneous, while below it, the reverse reaction (reduction) is spontaneous.

If all non H^+ species are at standard concentrations then the half
$E = E^o - 0.0592/n \log([H^+]^m) = E^o + m/n \cdot 0.0592pH$

c: $E = E^o - 0.0592/2 \log([H^+]^2) = E^o + 0.0592\ pH$
The slope is positive because $[H^+]$ is a product.

d: $E = E^o - 0.0592/2 \log([H^+]^{-2}) = E^o - 0.0592\ pH$
The slope is negative because $[H^+]$ is a reactant.

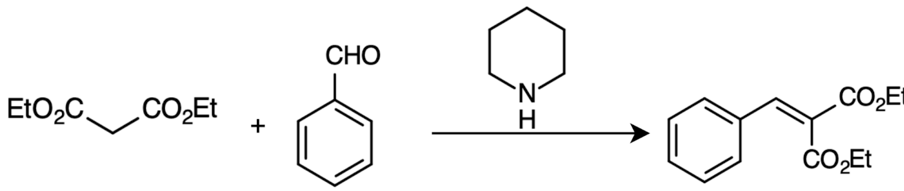
8-4 Write the reaction that occurs upon adding UCl_3 to a solution buffered at pH = 4.0

$2UCl_3 + 4H_2O \rightarrow 2UO_2 + 6H^+ + 6Cl^- + H_2$

8-5 Can $UO_2(CO_3)_3^{4-}$ and $U_4O_9(s)$ coexist between pH = 8-12? Can $UO_2(CO_3)_3^{4-}$ and $UO_2(s)$ coexist? Justify your answers.

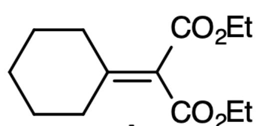
$UO_2(CO_3)_3^{4-}$ and $U_4O_9(s)$ can coexist between these pH values because their stability regions share a boundary (along which the two species can coexist).
$UO_2(CO_3)_3^{4-}$ and $UO_2(s)$ cannot coexist for the same reason.

Problem 9 [12%]
The Knoevenagel reaction is a useful type of condensation reaction. As shown in the figure below, diethyl malonate and benzaldehyde react in the presence of piperidine to form diethyl 2-benzylidenemalonate.



9-1 Draw the nucleophile in the reaction.

9-2 Briefly describe the role of piperidine
Piperidine is a base catalyst for the aldol/Knoevenagel condensation. It can also form an iminium ion with benzaldehyde rendering it more electrophilic.

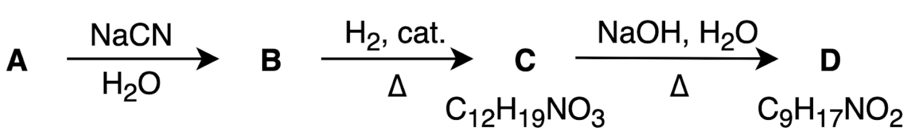


A

9-3 Compound **A** is a precursor to the anticonvulsant drug gabapentin **D**. Propose a synthesis of **A** using 2 organic reagents.

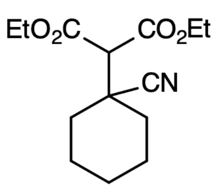
Cyclohexanone + Malonic Acid

Gabapentin (**D**) is synthesized as follows:

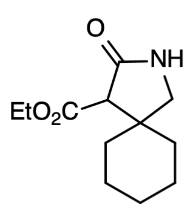


9-4 Draw the structural formulas of **B**, **C** and **D** in the above scheme.

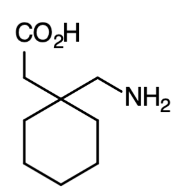
B



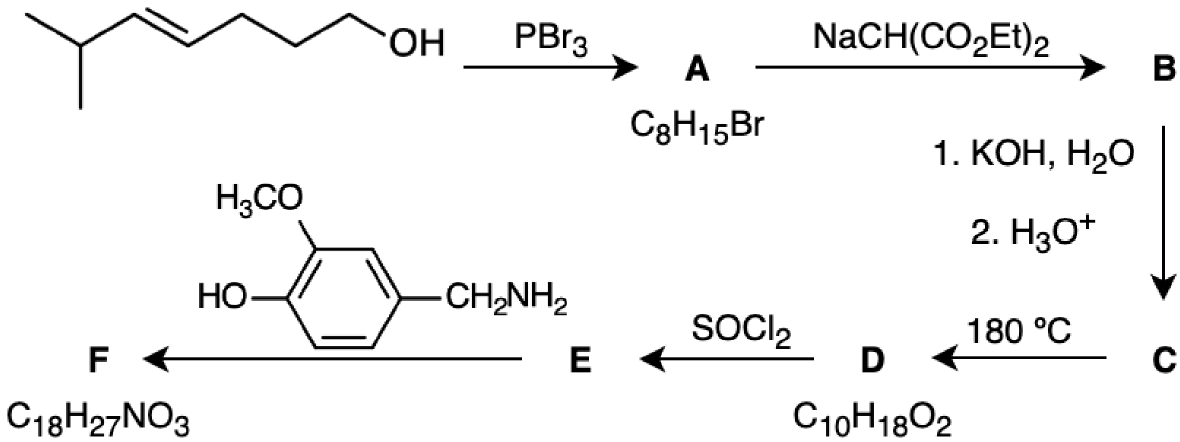
C



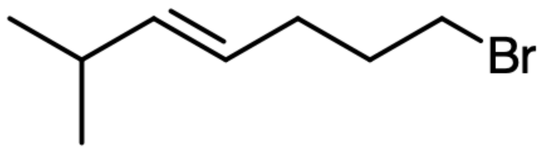
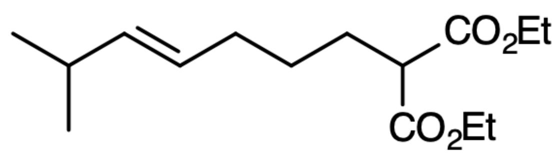
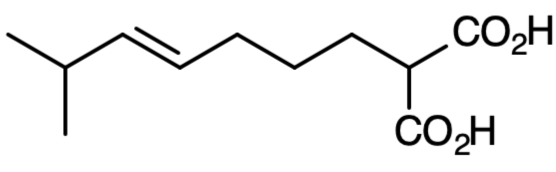
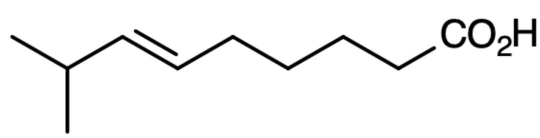
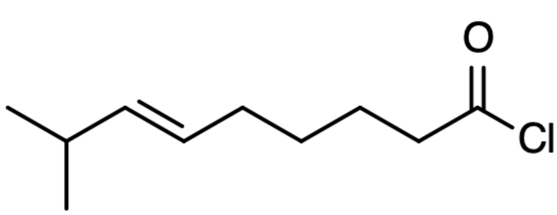
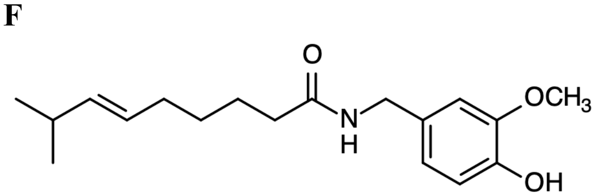
D



Problem 10 [6%]
The taste of pepper is mainly derived from capsaicinoids. The synthetic route of capsaicin **F** is shown below:

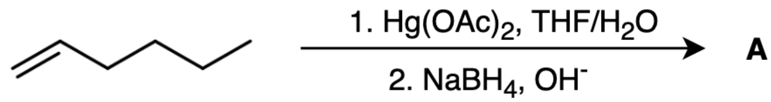


Draw the structural formulas of compounds **A**-**F**.

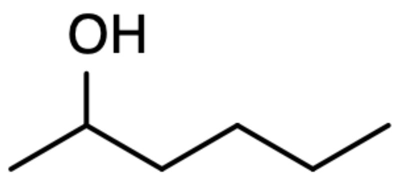
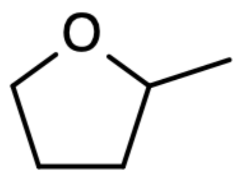
A 	**B** 
C 	**D** 
E 	**F** 

Problem 11 [12%]

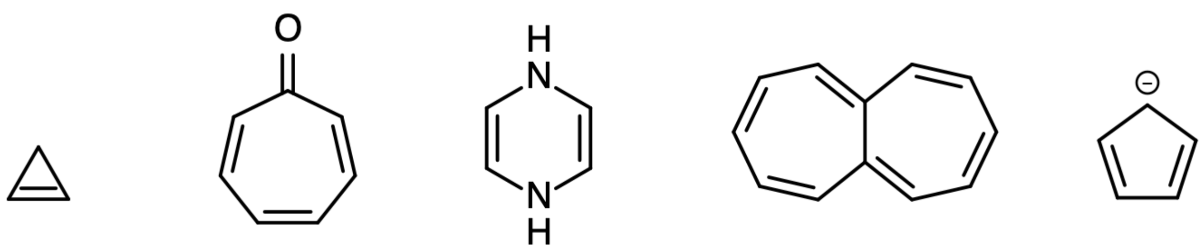
11-1 The oxymercuration-demercuration reaction of alkenes is similar to alkene bromination.



The main product formed when 4-penten-1-ol is reacted under the same conditions is **B**. Draw the structural formulas of **A** and **B**.

A	**B**
	

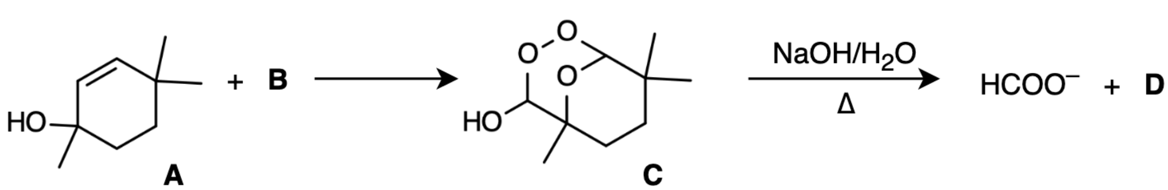
11-2 Which of the following organic compounds are aromatic?



1 2 3 4 5

2 and 5

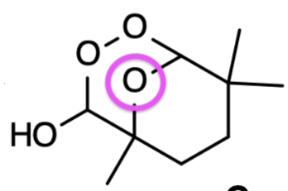
Compound **A** reacts in the following two steps to give compound **D**. Answer the following questions:



11-3 Write the formula for compound **B**

O_3

11-4 Circle the oxygen atom in **C** that came from **A**



C

11-5 Draw the structural formula of compound **D**.

D forms from an intermediate which undergoes an aldol condensation