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.

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:

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

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

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**, $\mathbf{AX_3}$ (a common Lewis acid), $\mathbf{A_2X_4}$ and $\mathbf{A_4X_4}$ can be generated.

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

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

$$\mathbf{AX_3}(g) \rightarrow \mathbf{AX}(g) + 2\mathbf{X}(g)$$
$$2Hg + 2\mathbf{X}(g) \rightarrow Hg_2\mathbf{X_2}(g)$$
$$\mathbf{AX}(g) + \mathbf{AX_3}(g) \rightarrow \mathbf{A_2X_4}(g)$$
$$4\mathbf{AX}(g) \rightarrow \mathbf{A_4X_4}(s)$$

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

A:	**X:**

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

2-3 Write the equation for the reaction of $\mathbf{AX_3}$ with CH_3MgBr in a 1:3 molar ratio.

2-4 Write the equation for the alcoholysis of $\mathbf{A_2X_4}$ by ethanol.

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).

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

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.

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

Problem 4 [5%]

Neutron diffraction experiments carried out in 1967 determined that there are only three ions in the crystal structure of trans-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$: $\mathbf{X}^+$, Cobalt-containing $\mathbf{A}^+$ and Cl^-. All atoms in $\mathbf{X}^+$ are coplanar. $\mathbf{X}^+$ also has a center of symmetry and three mirror planes that are perpendicular to each other. Note: en is an abbreviation for ethylenediamine.

4-1 Draw the structural formula of the stereoisomers of $\mathbf{A}^+$ and its stereoisomers

$\mathbf{A}^+$:	Stereoisomers

4-2 Draw the structural formula of $\mathbf{X}^+$.

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, $\beta = 98.13°$. 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 $g \cdot cm^{-3}$.

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

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).

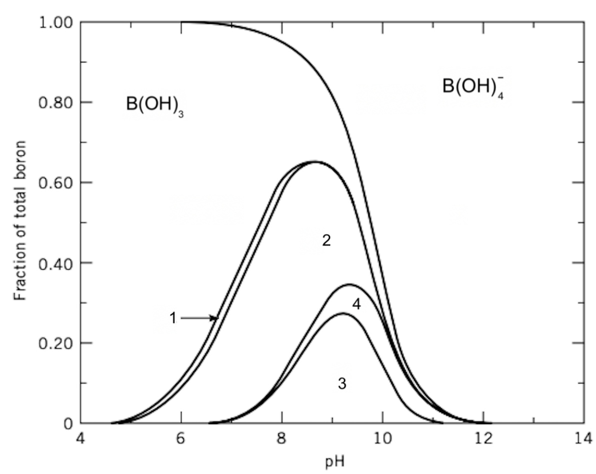
6-3 Draw the structure of niacin.

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.

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)

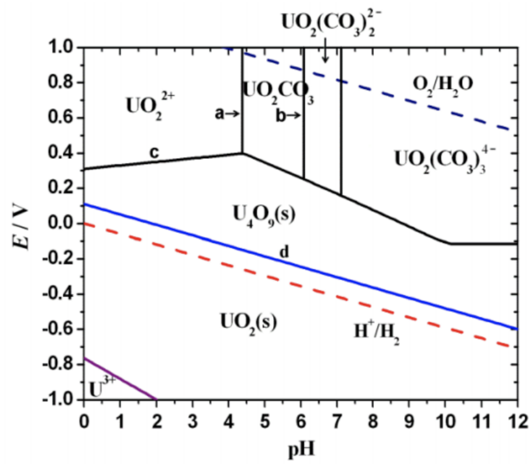
7-2 The figure on the right shows the relationship between the existence form and pH of the boric acid-borate system when the total concentration of boron is 0.4 mol L^{-1}. The numbered areas (labeled 1,2,3,4) between the curves represent the fractional composition of the 4 kinds of polyborate ions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



1:	2:
3:	4:

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

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.

a:

b:

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.

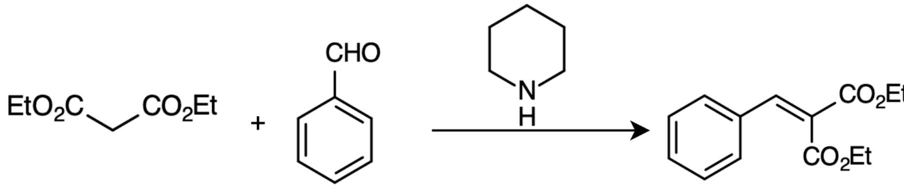
c:

d:

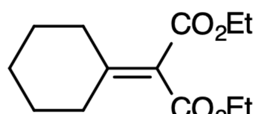
8-4 Write the reaction that occurs upon adding UCl_3 to a solution buffered at pH = 4.0

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.

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



A

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

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

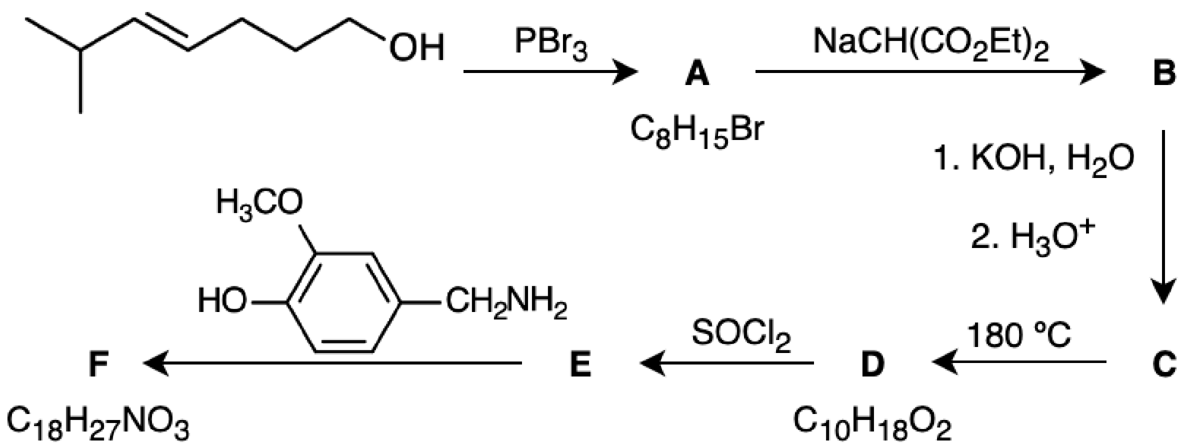
$$\mathbf{A} \xrightarrow[H_2O]{NaCN} \mathbf{B} \xrightarrow[\Delta]{H_2,\ cat.} \underset{C_{12}H_{19}NO_3}{\mathbf{C}} \xrightarrow[\Delta]{NaOH,\ H_2O} \underset{C_9H_{17}NO_2}{\mathbf{D}}$$

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:

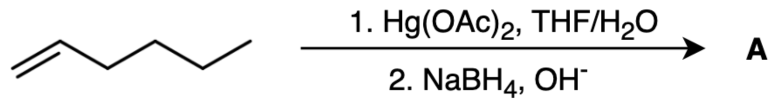


Draw the structural formulas of compounds **A**-**F**.

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

Problem 11 [12%]

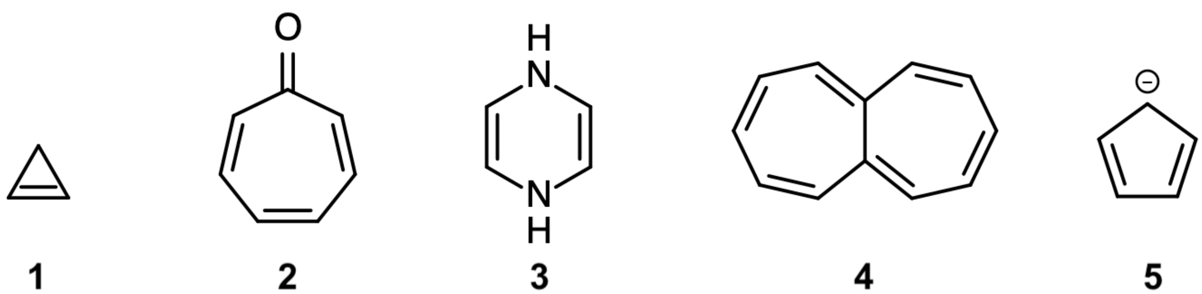
11-1 The oxymercuration-demercuration reaction of alkenes is similar to alkene bromination.



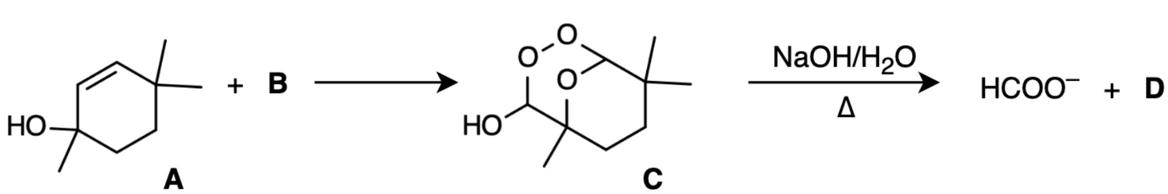
The main product formed when 4-penten-1-ol is reacted under the same conditions is **B**. Draw the structural formulas of **A** and **B**.

A	**B**

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

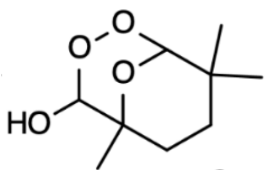


Compound **A** reacts in the following two steps to give compound **D**. Answer the following questions:



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

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



C

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