Chinese Chemistry Olympiad

2016

Question	1	2	3	4	5	6	7	8	9	10	Total
Points	8	9	13	10	8	14	8	10	12	8	100

EQUATIONS

$$E = E^{\circ} - \frac{RT}{nF}\ln Q \qquad \ln K = \left(\frac{-\Delta H^{\circ}}{R}\right)\left(\frac{1}{T}\right) + \text{constant} \qquad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

PERIODIC TABLE OF THE ELEMENTS

1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.008	2 2A																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	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	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)

Question 1 (8 points)

1.1 An ionic compound A_2B consists of four elements. One is hydrogen and the other three are all on the second period of the periodic table. Both positive and negative ions are composed of two distinct elements and both ions exist in a tetrahedral geometry. What is the chemical formula of this compound?

1.2 For the alkali metals Li, Na, K, Rb and Cs, which of the following properties is not monotonous (i.e. doesn't consistently increase or decrease) as the atomic number increases? Briefly explain the reasons.

(a) melting point
(b) atomic radius
(c) crystal density
(d) first ionization energy

1.3 $Na_2S_2O_4 \cdot 2H_2O$ is an important chemical product with a wide range of uses. It can be used to remove Cr(VI) from wastewater (pH~8). The Sulfur in the product is present as S(IV). Write the ion equation for the reaction

1.4 The results of chemical synthesis often take some time to be applied to daily life. For example, Compound **A** was synthesized in 1929 to 1969. Later, it was used as an additive for toothpaste and as a filler.
A is an ionic compound obtained by reacting NaF and $NaPO_3$ in a molten state. **A** is soluble in water and hydrolysis of its anion produces fluoride and another ion that is not toxic to humans.

1.4.1 Write the reaction for the synthesis of **A**.
1.4.2 Write the reaction for the hydrolysis of **A**.

Question 2 (9 points)

Presence of the nitrate anion, NO_3^- can be identified via the "brown ring" test.

To use the test, Iron (II) Sulfate is added to a solution containing NO_3^-. Next concentrated Sulfuric Acid is added along the tube wall. The high density of concentrated Sulfuric Acid causes the contents of the test tube to separate into two layers: H_2O and H_2SO_4. In the presence of nitrate, a brown ring will appear at the interface of the two layers. The formula of this brown ring was found to be $[Fe(NO)(H_2O)_5]SO_4$. The material is paramagnetic, with a magnetic moment of 3.87 μB (Bohr Magnetons) and unpaired electrons distributed in d orbitals around the center ion. Recall that the magnetic moment of a metal ion with n unpaired electrons is:

$$\mu = \sqrt{n(n+2)} \text{ (Bohr Magnetons)}$$

2.1 Write the net ionic equation for the formation of the brown ring in the given procedure.

2.2 Write the valence electron configuration and oxidation state of the central iron atom in $[Fe(NO)(H_2O)_5]SO_4$. Also, state whether the iron is low or high spin.

2.3 Compare the bond length of the NO bond in $[Fe(NO)(H_2O)_5]SO_4$ to that of a free NO bond. Briefly explain your reasoning.

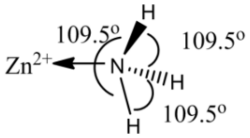
Question 3 (13 points)

3.1 P_2O_3 and P_2O_5 are two classical compounds whose molecular structure has been determined. However, compounds with a phosphorus-oxygen atomic ratio between P_2O_3 and P_2O_5 were not well known. Chemists then synthesized and confirmed the existence of such intermediate compounds.

3.1.1 Write the molecular formula of these intermediate compounds

3.1.2 Draw a structural formula for the one compound of the above which contains only one symmetry axis. Compare the bond angles for the phosphorus atoms in different oxidation states (O-P(V)-O vs O-P(III)-O)

3.2 In a single NH_3 molecule, the H-N-H bond angle is 106.7º, while in the $Zn(NH_3)_6^{2+}$ ion shown below, the measured H-N-H bond angle becomes 109.5º.



Explain this observation

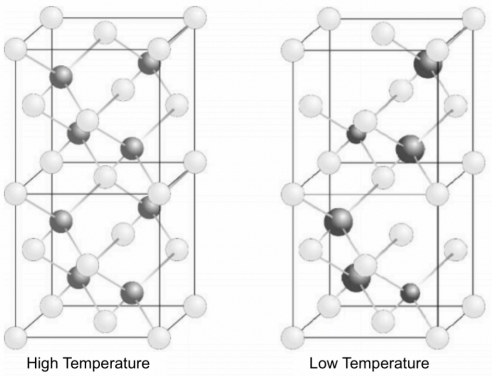
3.3 Quantum chemistry computations can be used to evaluate the stability of potential compounds. In February 2016, it was predicted that iron can form a tetraoxide with a tetrahedral molecular geometry. However, the oxidation state of iron in this compound is +6 and not +8.

3.1.1 Write the valence electron configuration of Iron in the molecule.

3.1.2 Draw a structural formula of a single molecule of the FeO_4

Question 4 (10 points)

A particular inorganic solid electrolyte is composed of positive ions A^{n+} and B^{m+}, and negative ions X^{-}. The substance forms a disordered structure (high temperature phase) above 50.7ºC and becomes ordered (low temperature phase) below 50.7ºC.



In the figure, the white spheres represent negative ions. In the high-temperature phase the black spheres are either positive ions or vacancies. In the low-temperature phase the large black spheres are A^{n+} ions, and the small black spheres are B^{m+} ions.

4.1 Determine the chemical formula of the electrolyte

4.2 Temperature changes cause crystals to switch between cubic and tetragonal systems. Which of the above crystal structures belongs to the cubic system

4.3 What crystal structure is formed by the negative ions and what kind of holes (tetrahedral or octahedral) are the positive ions occupying within the anionic lattice? How many of those holes are occupied?

4.4 The high temperature phase has good ionic conductivity, which originates from migration of which ion in the lattice? Briefly describe the relationship between electrical conductivity and structure to justify your answer.

Question 5 (8 points)

A mysterious oxidizing compound has chemical formula MO_xCl_y, where M is a transition metal, and x and y are positive integers. It is analyzed as follows:

A 2.9050 g sample of MO_xCl_y is added to a 100 ml flask and diluted to the mark. Next a 20.00 ml aliquot of the solution is taken. Dilute nitric acid and a sufficient amount of $AgNO_3$ is added, and 1.4360 g of a white precipitate was removed and weighed. Next another 20.00 ml aliquot of the solution is taken. An appropriate amount of sulfuric acid and an appropriate indicator are added. The solution is titrated with 3.350 mmol of ammonium ferrous sulfate solution. It is known that the cation exists as MO_x^{y+}.

Determine the identity of metal M and the formula of MO_xCl_y. Write the reaction for the titration of MO_x^{y+} with ammonium ferrous sulfate

Question 6 (14 points)

Interconversion of N_2O_4 and NO_2 is a common system for discussing chemical equilibrium. The reaction is as follows:

$N_2O_4\ (g) <=> 2\ NO_2\ (g)$ $\quad$ Kp = 0.100….(295 K)
$\quad$ Kp = 0.400….(315 K)

Some amount of N_2O_4/NO_2 mixture is added to a movable piston that maintains a constant pressure of 1 bar=1000 kPa.

6.1 Calculate the partial pressures of N_2O_4 and NO_2 in the piston at 295 K

6.2 Calculate the partial pressures of N_2O_4 and NO_2 in the piston upon heating to 315 K

6.3 Calculate the ratio of the total number of moles of gas at 315 K to the total number of moles of gas present at 295 K

6.4 As the temperature is increased to infinity, the value of Kp goes to infinity. Assuming no side reactions occur, what is the maximum value of P_{NO2}? Note: you must mathematically justify your answer. An answer with no justification will receive no more than 1 point

6.5 The temperature of the above system is raised from 295K to 315K under constant external pressure. Which of the following statements is correct:

(a) System shifts to the left
(b) System does not shift
(c) System shifts to the right
(d) All three are possible

6.6 Which of the following is true of the degree to which the equilibrium shifts under constant pressure compared to constant volume when the temperature is increased from 295 to 315 K under these conditions? (no calculation required)

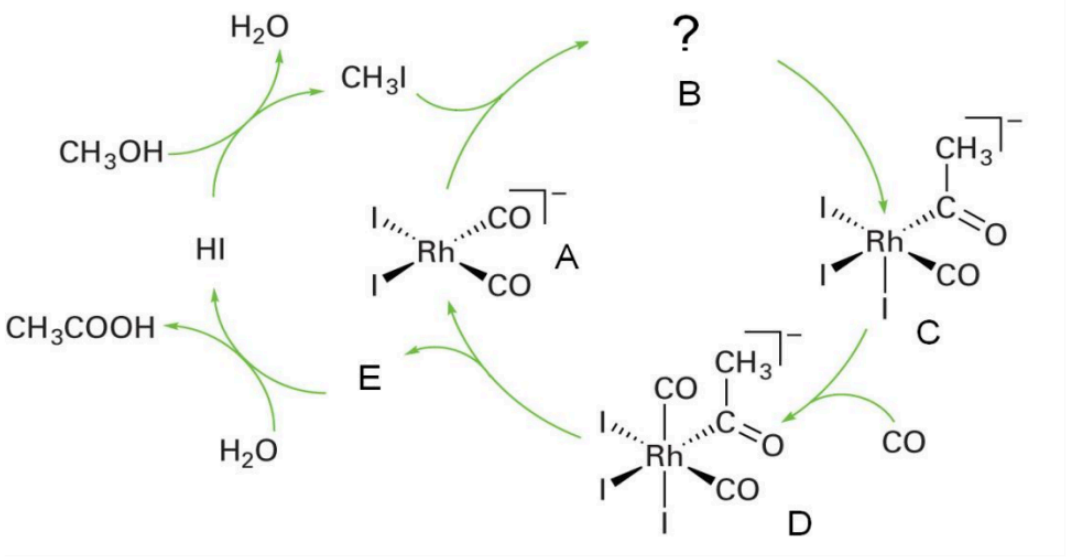
(a) Greater
(b) Smaller
(c) The same
(d) All three are possible

Question 7 (8 points)

The oxidation of ethanol by air under the action of acetic acid bacteria is an effective method for the manufacture of acetic acid, however, this traditional process is far from meeting the needs of the industry.

At present, industrially, methanol and carbon monoxide are mostly used to prepare acetic acid: $CH_3OH + CO \rightarrow CH_3COOH$. Some organometallic compounds of the Group 9 element (Co, Rh, Ir) are good catalysts for the above reactions.

For example $[Rh(CO)_2I_2]$ can be used in the synthesis of acetic acid with iodomethane as a promoter (Monsanto). The schematic diagram of the cycle is as follows:



7.1 In the catalytic cycle, A and methyl iodide undergo an oxidative addition reaction and become B. Draw a schematic diagram of the structure of B and its geometric isomers B_1-B_n. (n is the number of other geometric isomers)

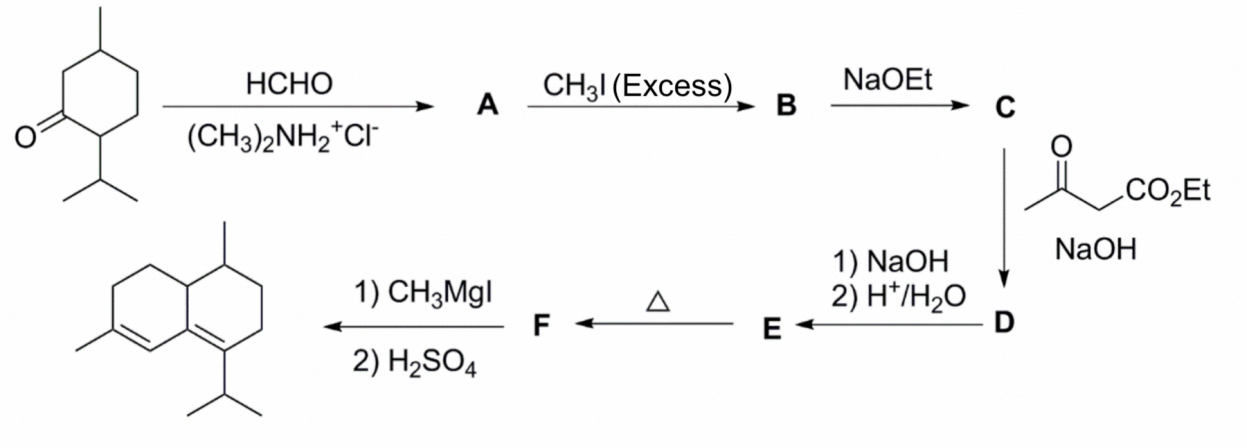
7.2 Give the oxidation states of the ruthenium in compounds A and D and their d electron count (ie d^{10} etc.)

7.3 Using condensed structural formulas, write the reaction formula for the production of acetic acid from E.

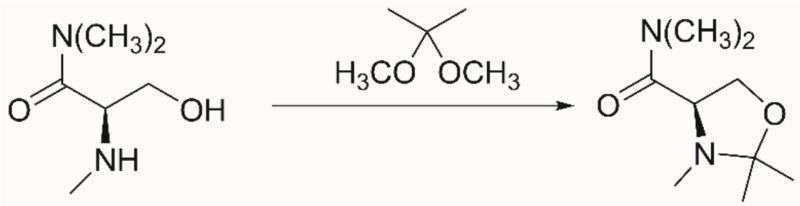
7.4 The Cativa method uses $[Ir(CO)_2I_2]$ for the given synthesis.
The method is similar, but the intermediates C and D (the center ions are Ir) differ because the transformation from B (center ion is Ir) to C, involves a CO ligand exchanging with an Iodide ligand. Draw the structure of C for the Cativa process and give its oxidation state.

Question 8 (10 points)

8.1 Draw the structures of compound A-F in the following reaction



8.2 A student designed the following reaction, hoping to protect both the amino group and the hydroxyl group.



Please select the experimental conditions that are most conducive to achieving this reaction:

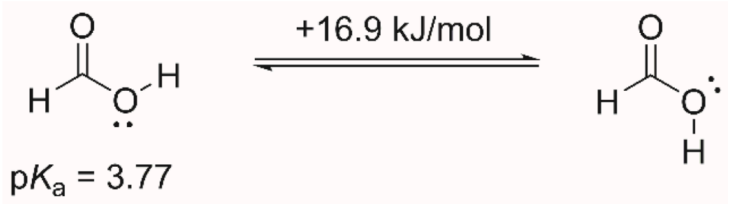
a) The reaction is carried out by heating in a mixed solvent of concentrated hydrochloric acid and ethanol (1:3).

b) The reaction is carried out by heating in an excess of triethylamine.

c) The reaction is carried out in anhydrous diethyl ether under catalytic loading of boron trifluoride.

d) The reaction is carried out in refluxing toluene.

8.3 Theoretical calculations show that there are certain energy differences between the Z and E-type isomers of formic acid.



The pKa of the Z-isomer is known to be 3.77, and the pKa of the E-isomer is:

a) > 3.77;

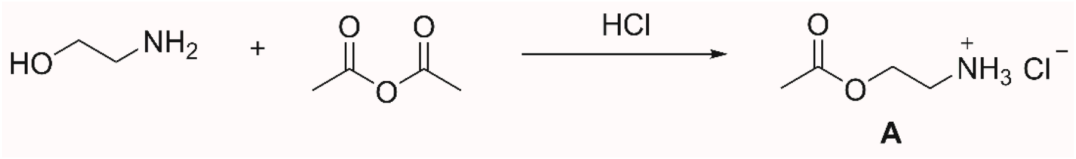
b) < 3.77;

c) = 3.77;

d) Cannot be decided with the given information

Question 9 (12 points)

9.1 Aminoethanol is reacted with acetic anhydride in hydrochloric acid as follows:



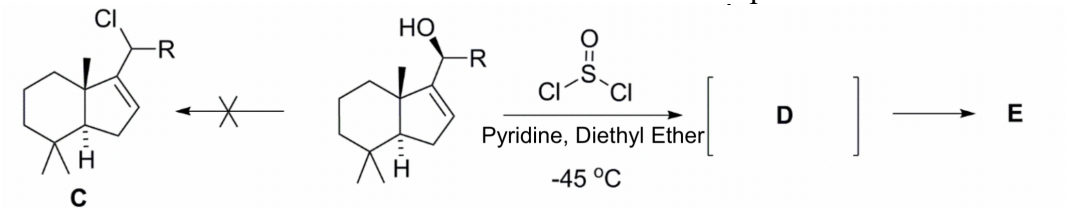
When this reaction is carried out in K_2CO_3, another acyclic product **B** is obtained. **A** is also converted to compound **B** upon reaction with K_2CO_3.

9.1.1 Draw the structure of compound **B**

9.1.2 Why does aminoethanol react with acetic anhydride to form **A** under HCl and **B** with K_2CO_3?

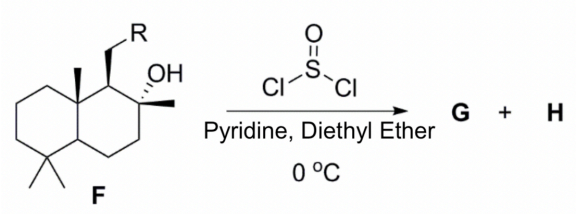
9.1.3 Why does **A** convert to **B** upon reaction with K_2CO_3

9.2 A student designed the following reaction conditions to prepare compound **C**. However, the isomer **E** was obtained instead after the reaction was completed



9.2.1 Draw the structures of important reaction intermediate **D** and **E**

In the following reaction, when compound **F** is reacted with thionyl chloride in a pyridine-diethyl ether solution, two isomeric products **G** and **H** containing a carbon carbon double bond and no chlorine were obtained. A third potential isomer **J** was not formed.



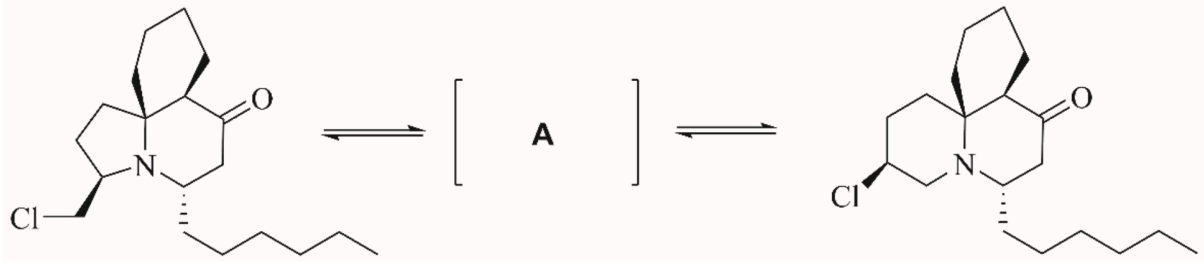
9.2.2 Draw the structures of **G**, **H**, and **J**.

9.2.3 Explain why product **J** is not obtained in the above reaction.

9.2.3 Draw the structures of **G**, **H**, and **J**.

Question 10 (8 points)

10.1 The following two alkaloids can be converted to each other at room temperature, and when the equilibrium state is reached, the ratio of the two is 3:2 The mechanism involves somewhat strained intermediate. Draw the structure of this key intermediate.



10.2 The following transformation involves a highly strained 3 membered ring reaction intermediate. Draw the structures of the key intermediates in the transformation.