2015 CChO National Round

47TH
INTERNATIONAL
CHEMISTRY OLYMPIAD
BAKU, AZERBAIJAN 2015

This test paper consists of 9 questions with a total score of 100 points
The test time is 4 hours

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	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%]

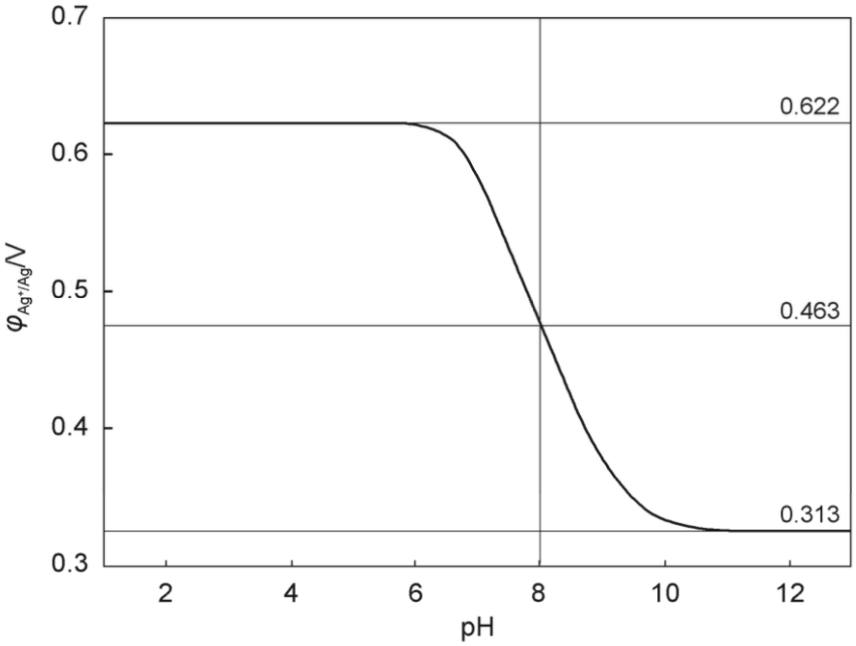
1-1 CH_3SiCl_3 reacts with sodium metal in liquid ammonia to obtain a molecule with formula $Si_6C_6N_9H_{27}$. This molecule has a threefold symmetry axis, and all Si atoms are indistinguishable. Draw the 3D structure of the molecule and write a balanced equation for the reaction forming $Si_6C_6N_9H_{27}$.

1-2 Sodium metal reacts with $(C_6H_5)_3CNH_2$ in liquid ammonia to produce a red sodium salt. Write the balanced equation and explain why the product is red.

1-3 It was recently found that under high pressure Cs can form CsF_5 molecules containing a single central atom. Using VSEPR theory, explain the electron pair distribution of CsF_5 and propose a plausible structure.

Problem 2 [11%]

A silver electrode was placed in a mixed solution of 1.000×10^{-1} mol·L^{-1} NH_4NO_3 and 1.000×10^{-3} mol·L^{-1} $AgNO_3$ at 298 K, and the electrode potential φ(Ag^+/Ag) was measured as a function of pH of the solution as shown below. It is known that the dissociation constant K_b of ammonia is 1.780×10^{-5}, the ideal gas constant R = 8.314 J·mol^{-1}·K^{-1}, and the Faraday constant F = 96500 C·mol^{-1}.



2-1 Calculate the standard electrode potential φ°(Ag^+/Ag) of the silver electrode at 298 K

2-2 Calculate the stepwise stability constants $K_1°$ and $K_2°$ of the silver-ammonia complex ion

2-3 A primary battery is designed using the coordination reaction of silver ions. The battery reaction is:

$$Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$$

Calculate the standard emf of the battery. If you could not compute the stability constants of the primary and secondary ions of the silver ammonia complex, assume they are both $1.00\cdot10^3$

Problem 3 [12%]

CuO and $Ba(NO_3)_2$ are mixed in a 1:1 molar ratio. The mixture is heated and dissolved in dilute nitric acid. The obtained solution is freeze dried into small particles and dried at low temperature. After drying, the material is transferred to a platinum crucible with a 1.0×10^5 Pa oxygen atmosphere where it was heated to 620°C and held for 18 hours to obtain a mixture of solid substances **A** and **B**, and substances **A** and **B** were separated.

Elemental and structural analysis shows that substance **A** is composed of three elements: Ba, Cu, and O. In the structure of **A**, Oxygen forms long chains of linear quadrilaterals connected along opposite edges with Cu atoms located in the center of each quadrilateral. Barium is located between the quadrilaterals. 1.00 g of **A** was added to a solution containing excess amount of potassium iodide and 3 $mol\cdot L^{-1}$ hydrochloric acid was added dropwise under an argon atmosphere until the solid was completely dissolved to obtain a solution **S** (Reaction 1). Solution **S** was diluted with water to obtain white precipitate **C** (Reaction 2); Solution **S** was titrated with 0.100 $mol\cdot L^{-1}$ sodium thiosulfate solution to a starch endpoint consuming 44.54 mL (Reaction 3). If **A** is first dissolved with hydrochloric acid (Reaction 4), and then slowly added to a solution containing excess potassium iodide (Reaction 5), a solution containing precipitate **C** is directly obtained. The solution is titrated with 0.100 $mol\cdot L^{-1}$ sodium thiosulfate solution, consuming 26.72 mL .

Substance **B** was slowly heated to 820 °C under a 20% oxygen 80% nitrogen atmosphere resulting in a mass loss of 9.45% (Reaction 6) to obtain substance **D**. Upon slowly cooling to 400 °C, the solid returned to its original weight.

3-1 Write the chemical formulas for **A**, **B**, **C** and **D**.

3-2 Write balanced net ionic equations for each numbered reaction.

3-3 In the above titrations, a small amount of KSCN is often added close to the endpoint to improve the accuracy of the titration. Explain how KSCN improves the accuracy of the titration, and why it must be added only at the end of the titration.

Problem 4 [14%]

Hydrogen is most likely to be the main energy source in the 21st century, but hydrogen needs to be prepared from other substances. One of the methods for producing hydrogen uses coal and water. Hydrogen is produced by the following reactions between carbon and water occurring in a gasifier.

(1) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
(2) $CO(g) + H_2O\ (g) \rightleftharpoons CO_2(g) + H_2(g)$

CaO is added to absorb the CO_2 formed

(3) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

The H_2 in the product reacts with C, CO, CO_2 in the equilibrium system to produce CH_4:

(4) $C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$
(5) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
(6) $CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g)$

2 mol C(s), 2 mol $H_2O(g)$, 2 mol CaO(s) are added into a gasifier and heated to 850 ºC

Thermodynamic data for the relevant compounds at 850 ºC

Compound	$\Delta_f H_m{}^o$ / (kJ·mol^{-1})	$S_m{}^o$ / (J·mol^{-1}·K^{-1})
C(s)	8.70	21.04
CO(g)	-93.65	229.22
$CO_2(g)$	-368.10	260.49
CaO(s)	-606.97	90.58
$CaCO_3(s)$	-1147.40	196.92
$H_2(g)$	16.21	161.08
$H_2O(g)$	-221.76	226.08
$CH_4(g)$	-46.94	236.16

4-1 Calculate the mole fraction of H_2 in the final gas mixture at equilibrium given that the total pressure of the gasifier is 2.50×10^6 Pa at equilibrium.

4-2 Calculate the amount of heat transferred from the starting mixture to reach equilibrium.

4-3 Carbon is an excellent reducing agent at high temperatures and can be used to smelt many metals. Write the chemical formulas of the possible oxidation products of carbon at 600 ºC. Determine which oxidation product is most prevalent at 600 ºC (assume the entropy change and enthalpy change at 600 °C are the same as at 850 °C)

Problem 5 [14%]

MAX (**M** stands for transition metal elements, **A** stands for a main group element, **X** stands for carbon or nitrogen) is a new type of ceramic material that has attracted much attention. Due to its unique layered crystal structure, it has self-lubricating properties, high toughness, and electrical conductivity, and can be used for high-temperature structural materials, electrode materials, and anti-corrosion materials. One **MAX**-phase material contains Ti, Al, and N atoms and belongs to the hexagonal crystal system. The underlying structure involves layers of hexagonally packed Ti atoms stacked in a ...BACBBCABBACBBCAB… fashion. N atoms occupy all of the octahedral holes, while Al atoms occupy half of the triangular prism holes. If a Ti layer is adjacent to a layer of N atoms and a layer of Al atoms, the projections of Al and N atoms coincide along the z-axis (normal to the layers of Ti atoms) of the unit cell.

5-1 Determine the chemical formula of the compound, and state the number of each kind of atom in its unit cell

5-2 Along the unit cell z axis an imaginary straight line is drawn through the Al and N atoms. List at least 10 atoms in the order they lie on this line.

5-3 It is known that the average bond length between Ti and N atoms is 210.0 pm, and the average bond length between Ti and Al atoms is 281.8 pm. Compute the theoretical density of the crystal.

5-4 The grain size will affect the properties of the above materials, so the grain size is generally increased by holding the samples at high temperature for longer. Predict whether the entropy, enthalpy, and free energy changes of the grain growth process at 25 ºC are positive or negative, and determine whether the grain growth process is spontaneous at 25 ºC.

5-5 The above descriptions are for perfect crystals. In general, defects will occur in the grains. Justify using thermodynamics that for a sufficiently large crystal, the formation of defects is spontaneous.

Problem 6 [12%]

Heterogeneous catalytic reactions where the reaction system is gas and the catalyst is solid are common. Suppose the gas is adsorbed in a single layer on the surface of a uniform solid catalyst, the energy of adsorption to each active site is the same, the interaction between the adsorbed particles is ignored, and the adsorption equilibrium constant does not change with pressure.

6-1 At 180 K with partial pressure of 3.50×10^5 Pa, ideal gas **X** can adsorb onto 1g of solid catalyst with adsorption capacity of 1.242 cm^{-3}. In order to reach the same adsorption capacity at 240 K, the pressure needs to be increased to 1.02 mPa. Estimate the molar enthalpy of adsorption of **A** onto the surface of the catalyst (assume that the molar adsorption enthalpy is constant within this temperature range).

6-2 The reaction **A**(g) → **B**(g) with rate constant k_2 has the mechanism:

$$\mathrm{A(g)} + * \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} \mathrm{A}^* \xrightarrow{k_1} \mathrm{B(g)} + *$$

where * stands for an active site on the catalyst surface. Each active site can only accommodate a single adsorbed **A*** molecule at any given time. The conversion of **A*** to **B** is the rate determining step. The concentration of the adsorbed form **A*** is expressed by the surface coverage (written as the fraction of total active sites occupied by **A***). The rate constant k_2 for **A**(g) → **B**(g) was measured at 298 K. At high pressures the rate constant was 5 $\mathrm{kPa \cdot s^{-1}}$ and at low pressures it was 0.1 $\mathrm{s^{-1}}$. Calculate the reaction rate when the partial pressure of **A** is 50 kPa.

6-3 If product **B** can also undergoes adsorb to the surface, the reaction mechanism becomes:

$$\mathrm{A(g)} + * \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} \mathrm{A}^* \xrightarrow{k_1} \mathrm{B}^* \underset{k_\mathrm{a1}}{\overset{k_\mathrm{d1}}{\rightleftharpoons}} \mathrm{B(g)} + *$$

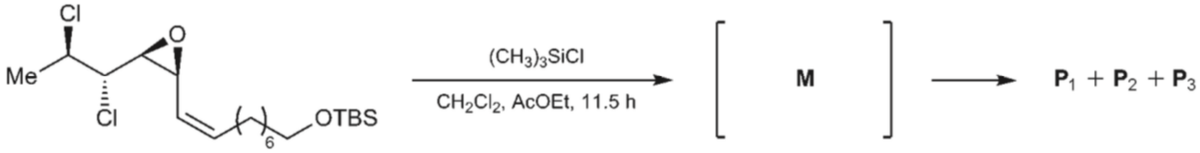
In this case, the rate determining step is the conversion of **A*** to **B***. Assume that k_a, k_d, k_1 have the same values as in question **6-2**. When the partial pressure p_B of product **B** is much greater than p_A, the overall reaction

$$\mathbf{A(g)} \xrightarrow{k_3} \mathbf{B(g)}$$

is first-order in **A** and the rate constant k_3 can be expressed as a function of p_B: $k_3 = 10/p_B$ $\mathrm{kPa \cdot s^{-1}}$. Calculate the equilibrium constant for the absorption of **B**(g) to the catalyst: $K_B = k_{a1}/k_{d1}$.

Problem 7 [9%]

Marine organisms contain many biologically active substances. Ingestion of certain seafood can cause serious food poisoning. Total synthesis research of cytotoxin chlorosulpholipid shows that the polychlorinated structure contained in the molecule is of great significance to its biological activity. In this molecular synthesis route, the introduction of chlorine atoms leads the epoxide ring-opening reaction shown below (TBS = t-Bu$(CH_3)_2$Si):



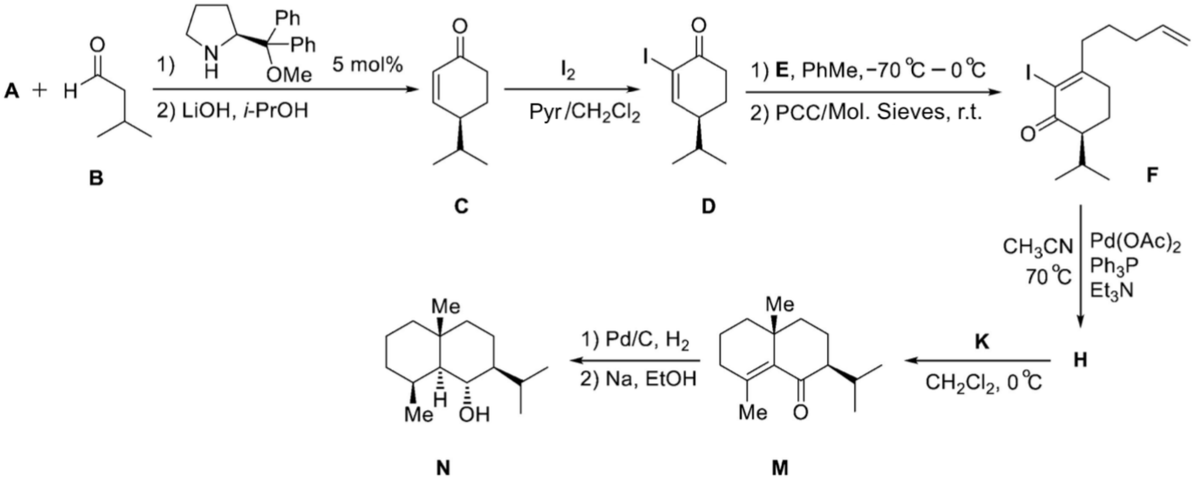
Using dichloromethane and ethyl acetate as solvents, three ring-opening products $\mathbf{P_1}$, $\mathbf{P_2}$ and $\mathbf{P_3}$ were obtained.

7-1 Draw the structural formula of intermediate **M**.

7-2 Draw the structural formulas of **P1**, **P2**, and **P3**, and the mechanisms forming each.

Problem 8 [11%]

The following is a fragment of the synthetic route of the natural product terpenoid eudesmane ("r.t." is room temperature, and PCC is CrO_3 / pyridine / hydrochloric acid):



8-1 Draw the most stable conformation of the product **N**.

8-2 Draw structural formulas for reagents **E**, **K** and intermediate **H**.

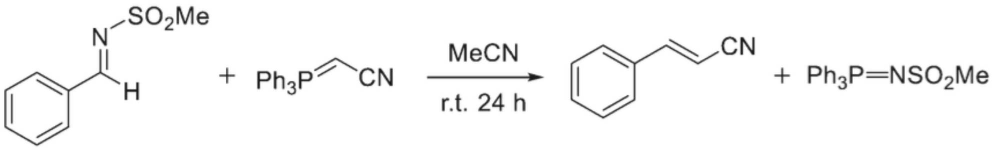
8-3 Draw the structural formula of the intermediate in the conversion of **M**→**N**

8-4 Perform retrosynthetic analysis on the intermediate **C** (stereochemistry not required) and determine the structure of **A**

8-5 Draw the key intermediates in the mechanism for the formation of **C** to explain the stereoselectivity of the step.

Problem 9 [10%]

In 19953 Wittig reported that phosphonium ylides (also known as Wittig reagents) reacted with aldehydes and ketones to directly convert the carbonyl group into a carbon-carbon double bond, and at the same time produced the by-product triphenylphosphine oxide. The so-called Wittig reaction is an important way of making carbon-carbon double bonds. One study in the literature examined the following variant of the Wittig reaction.



9-1 Give the configuration of the C=N double bond (Z or E) in the reactant.

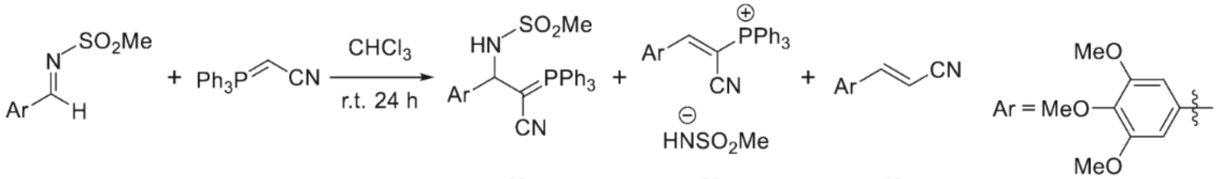
9-2 Draw the resonance structure of Ph_3P=CHCN.

9-3 Indicate which of the following ^{1}H NMR spectrum information can be used to determine the C=N double bond configuration of the reactant.

I. Chemical shift II. Magnetic anisotropy III. Shielding effect IV. NOE effect

9-4 Explain the effect of the —SO_2Me group in the reactant structure on the reaction.

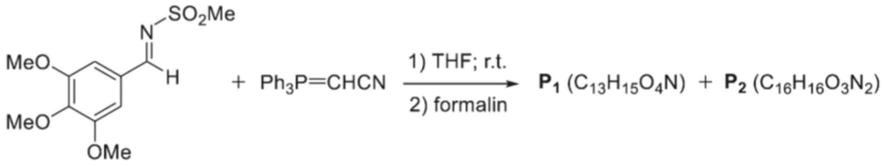
9-5 When studying the above reaction mechanism, the following reactions were discovered:



M$_1$ **M$_2$** **M$_3$**

Draw the mechanisms for the formation of **M$_2$** and **M$_3$**

9-6 If the reaction from **9-5**, is carried out at room temperature using tetrahydrofuran (THF) as the solvent, and then quenched with formalin (aqueous solution of formaldehyde), two products **P$_1$** and **P$_2$** are formed



Draw the structures of **P$_1$** and **P$_2$**.

9-7 The Wittig reaction is generally carried out in an aprotic polar solvent, but in **9-6**, formalin is used to quench the reaction to obtain the products **P1** and **P2**. Draw the structures of the key intermediates leading to the formation of **P$_2$**.

The problems and their solutions (In Chinese) can be found in the "Journal of Physical Chemistry" and "University Chemistry" at Peking University:
http://www.dxhx.pku.edu.cn/EN/Y2016/V31/I2/46