54th IChO2022 QUESTIONS and MARKING SCHEMES

中国·天津

54th IChO2022
International Chemistry Olympiad

TIANJIN, CHINA

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International Chemistry Olympiad 2022 Tianjin, China

54th IChO2022 Tianjin, China

10th July –18th July, 2022

https://icho2022.cn/

CHANGE CREATION FUSION

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International Chemistry Olympiad

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General Instruction

- This examination has **9 problems**.

- Use only a pen and non-programmable calculator.

- You have **5 hours** to complete the exam.

- **Begin** only when the **START** command is given.

- All results must be written in the appropriate boxes with a pen on the **answer sheets**. Use the back of the exam sheets if you need scratch paper. Remember that the content of the answer boxes will be graded.

- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.

- The invigilator will announce a **30-minute** warning before the **STOP** command.

- You **must stop** working when the **STOP** command is given. Failure to stop writing will lead to the nullification of your exam.

- The official English version of this examination is available on request only for clarification.

- You are not allowed to leave your working place without permission. If you need any assistance (broken calculator, need to visit a restroom, etc.), raise hand and wait until an invigilator arrives.

- **For questions where you are asked to choose from a collection of choices, indicate your answer with a ✓ in the [ ] before your choice.** An example is provided below:

  (Suppose you wish to choose (A) out of (A), (B), (C) and (D).)

  [✓] (A)   [ ] (B)   [ ] (C)   [ ] (D)

GOOD LUCK!

Problems and Grading Information

No	Title	Total Points	% of Total
1	Rapid and Visual Nucleic Acid Testing for COVID-19	14	9
2	Chromium in Ancient and Modern Times	21	11
3	Capture and Transformation of Carbon Dioxide	42	14
4	A New Journey for Ancient Sulfur	45	16
5	Interconversion among Nitrogen Oxides	45	15
6	Enabling Phosphines	36	7
7	Organic Molecules in Life	32	9
8	Amazing Chiral Spiro Catalyst	36	10
9	Total Synthesis of Capitulactone	44	9
	Total		100

Physical Constants and Equations

Avogadro constant:	$N_A = 6.022 \times 10^{23}\,\mathrm{mol}^{-1}$
Universal gas constant:	$R = 8.31446\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$
Standard pressure:	$p^{\ominus} = 1\mathrm{bar} = 10^5\,\mathrm{Pa}$
Standard atmospheric pressure:	$p_{\mathrm{atm}} = 1\,\mathrm{atm} = 1.01325\,\mathrm{bar} = 1.01325 \times 10^5\,\mathrm{Pa}$
Zero of the Celsius scale:	273.15 K
Faraday constant:	$F = 9.6485 \times 10^4\,\mathrm{C\,mol}^{-1}$
Planck's constant:	$h = 6.626 \times 10^{-34}\,\mathrm{J\,s}$
Mass of electron:	$m_e = 9.109 \times 10^{-31}\,\mathrm{kg}$
Speed of light:	$c = 2.998 \times 10^8\,\mathrm{m\,s}^{-1}$
pi:	$\pi = 3.141592653589793$

Energy of a photon:	$E = hc/\lambda$
Ideal gas equation:	$pV = nRT$
The first law of thermodynamics:	$\Delta U = Q + W$
Enthalpy H:	$H = U + pV$
The change of entropy:	$\Delta S = Q_{\mathrm{rev}}/T$
Gibbs free energy:	$G = H - TS$
	$\Delta G^{\ominus} = -RT\ln K^{\ominus}$
	$\Delta G^{\ominus} = -nFE_{\mathrm{cell}}^{\ominus}$
	$\Delta G = \Delta G^{\ominus} + RT\ln Q$
Reaction quotient: *For a reaction* $\mathrm{a[A] + b[B] \rightleftharpoons c[C] + d[D]}$	$Q = \dfrac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$
Nernst equation:	$E = E^{\ominus} - \dfrac{RT}{nF}\ln\dfrac{c_{\mathrm{red}}}{c_{\mathrm{ox}}}$
Langmuir isotherm equation:	$\theta = aP/(1 + aP)$
Arrhenius equation:	$k = Ae^{-E_a/RT}$
Integrated rate law:	
Zero order:	$[\mathrm{A}] = [\mathrm{A}]_0 - kt$
First order:	$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$
Second order:	$\dfrac{1}{[\mathrm{A}]} = \dfrac{1}{[\mathrm{A}]_0} + kt$

Theory

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G0-5

English (Official)

Half-life time for a first order process:	$t_{1/2} = \dfrac{\ln 2}{k}$
Half-life time for a second order process (A + A $\longrightarrow$ B):	$t_{1/2} = \dfrac{1}{k[\mathrm{A}]_0}$
Lambert–Beer equation:	$A = \varepsilon l C$
Electric work:	$W = UIt = UQ$
Quantity of electric charge:	$Q = It$
Volume of a sphere:	$V = \dfrac{4}{3}\pi r^3$
Surface area of a sphere:	$S = 4\pi r^2$

Theory

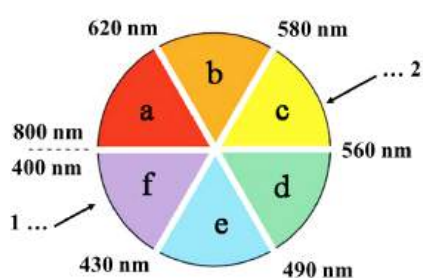54th IChO2022
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G0-6

English (Official)

Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	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 65.38	31 Ga 69.72	32 Ge 72.63	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 -	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	57–71	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 -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	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
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

The Color Wheel

a: red   b: orange   c: yellow   d: green   e: blue   f: violet
1: If a substance absorbs here   2: it appears as this color.

Figure 0.1

Theory

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Q1-1
English (Official)

Rapid and Visual Nucleic Acid Testing for COVID-19

9% of the total						
Question	1.1	1.2	1.3	1.4	1.5	**Total**
Points	1	1	4	4	4	**14**
Score						

Fast and simple methods for early detection of COVID-19 are urgently needed. Gold nanoparticles-aided detection is one of the promising methods. Gold nanoparticles are widely used as a visible readout for test strips due to their high molar extinction coefficients (molar absorptivity). The color appearance of gold nanoparticles is closely associated with their sizes and dispersity. Generally, the larger the gold nanoparticles, the more reddish the color is. Once the nanoparticles are aggregated, the color shifts from red to blue.

When the surface of gold nanoparticles is modified with two kinds of single-stranded nucleic acid fragments a and b, the gold nanoparticles would aggregate in the presence of the target nucleic acid (a' b'), causing the color change of the solution from red to blue in several minutes (as indicated below). Based on this principle, the target nucleic acids collected from the coronavirus in a sample can be detected.

Dispersed (Red)   Aggregated (Blue)
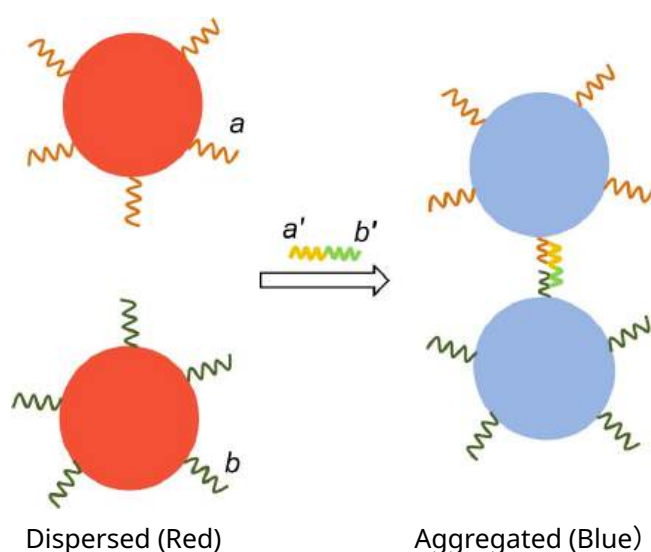
1.1	**Indicate** the absorption band region of the dispersed gold nanoparticles with an appropriate letter (a-f in the color wheel of **Figure 0.1** in **General Instructions**)	1.0 pt

Theory

Q1-2

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1.2	**Indicate** the change in the absorption spectrum of the gold nanoparticles once they are aggregated. Compared to the absorption wavelength of the dispersed gold nanoparticles, the wavelength of the aggregated nanoparticles (a) becomes longer (b) becomes shorter (c) does not change	1.0 pt

Gold nanoparticles are composed of gold atoms that are closely packed as solid gold (density $\rho = 19.3\,\mathrm{g\,cm^{-3}}$).

1.3	**Calculate** how many gold atoms (N) are there in a spherical gold nanoparticle with a **diameter** of 30.0 nm.	4.0 pt

The synthesis of gold nanoparticles depends on the redox reaction between hydrogen tetrachloroaurate(III) ($HAuCl_4 \cdot 3H_2O$, $M_W = 394$) and reducing substances (such as sodium citrate). 5.2 mg of $HAuCl_4 \cdot 3H_2O$ was completely converted into uniform spherical gold nanoparticles with a diameter of 30.0 nm in a 100.0 mL reaction solution. The absorbance of the resulting red solution was 0.800 measured at 530 nm by a UV-Vis spectrometer.

1.4	**Calculate** the molar extinction coefficient (molar absorptivity) of the resulting gold nanoparticles solution at 530 nm per mol of gold nanoparticles. The optical path of the cuvette used is 1 cm. If you failed to get the number of gold atoms (N) in **1.3** , use $N = 1.00 \times 10^5$.	4.0 pt

The standard addition method was used for colorimetric detection of the target nucleic acid. The original throat swab sample was collected and divided equally into two portions. After addition of the probe solutions and water (as indicated below), the absorbance of the two resulting solutions was measured at 600 nm separately.

No.	Volume of throat swab sample (mL)	Volume of solution of gold nanoparticles modified with nucleic acid fragments (mL)	Volume of standard solution containing 2.0 µg mL^{-1} target nucleic acid (mL)	Volume of water (mL)	Absorbance
1	0.10	0.80	0.00	0.10	0.400
2	0.10	0.80	0.10	0.00	0.900

1.5	**Calculate** the concentration of the viral nucleic acids in the original throat swab sample.	4.0 pt

Rapid and Visual Nucleic Acid Testing for COVID-19

9% of the total						
Question	1.1	1.2	1.3	1.4	1.5	**Total**
Points	1	1	4	4	4	**14**
Score						

1.1 (1.0 pt)

[   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)   [   ] (e)   [   ] (f)

1.2 (1.0 pt)

[   ] (a)   [   ] (b)   [   ] (c)

1.3 (4.0 pt)

$N =$ _____

1.4 (4.0 pt)

$\varepsilon =$ _____ $L\,mol^{-1}\,cm^{-1}$

1.5 (4.0 pt)

$c_X =$ _____ $\mu g\,mL^{-1}$

Theory

Q2-1

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English (Official)

Chromium in Ancient and Modern Times

11% of the total									
Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	**Total**
Points	2	1	6	1	2	1	1	5	2	**21**
Score										

(The photo is from the website of Palace Museum)

Black glazed porcelain is a special Chinese porcelain and was popular in the Tang and Song dynasties (ca. 1000 years ago). The ceramic ware contained iron oxides as the main color rendering agent, which was mixed with other transition metal oxides to exhibit different color appearance such as auburn, dark brown or black. Currently, the black glazed porcelain is still popular in China.

Theory

Q2-2

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The typical black glaze is composed of Fe-containing oxides with a spinel structure. Spinel oxides have the general formula AB_2O_4 and the structure consists of a cubic close packing array of O^{2-} ions in which the **A** cations occupy one-eighth of the tetrahedral vacancies and the **B** cations occupy half of the octahedral vacancies, as shown in **Figure 2.1**(a) for a unit cell.
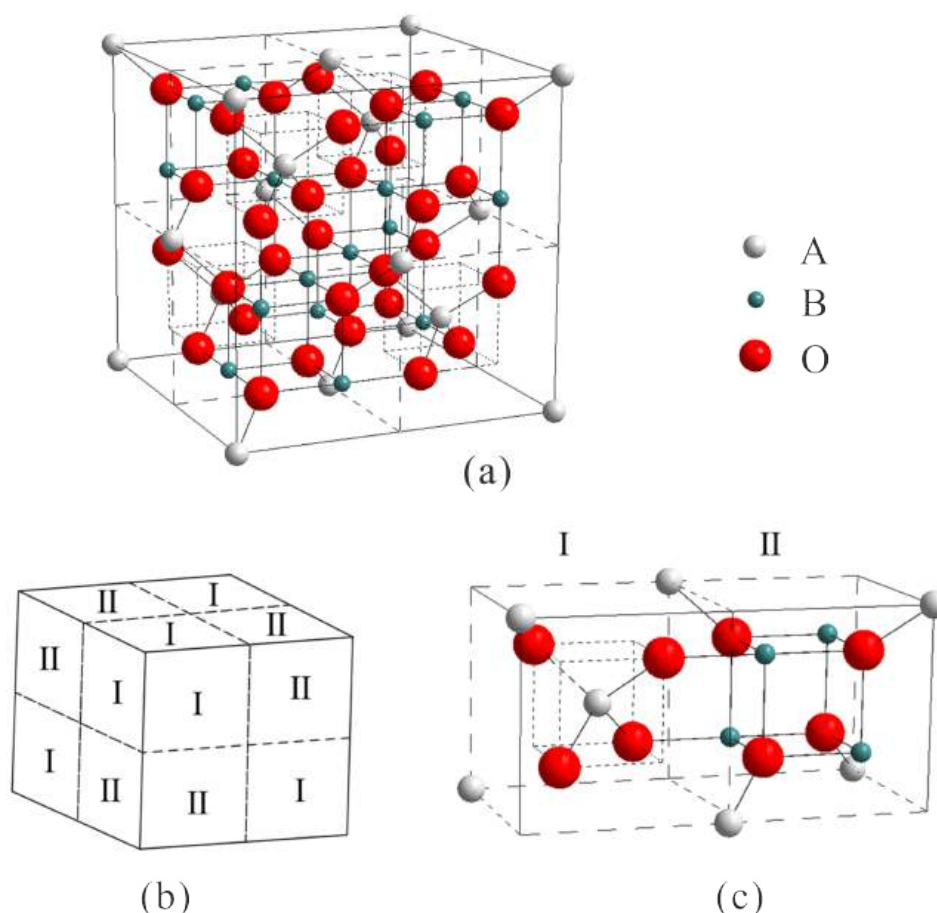
Figure 2.1 Illustration of spinel structure

The cubic unit cell of a spinel structure can be divided into 8 cubic subunits, and the dashed lines represent the internal edges of the subunits. 4 of the subunits belong to type I, and the other 4 subunits are type II (**Figure 2.1**(b)). The details of adjacent subunits of type I and type II are shown in **Figure 2.1**(c).

2.1	**How many** cations of type **A** and **B** are there in a unit cell?	2.0 pt

The black ceramic glaze with spinel structure can be produced by roasting Fe_2O_3 and Cr_2O_3 in a certain proportion in a reducing atmosphere (**reaction (I)**). When Fe_2O_3 and Cr_2O_3 are reacted with the mass ratio of 63.6 : 36.4, they completely transform into a pure stoichiometric compound. The product has a spinel structure, in which the tetrahedral **A** sites are occupied by iron cations only.

2.2	In **reaction (I)**, **which element** is reduced?	1.0 pt

2.3	**Calculate** the numbers of Fe^{3+} and Cr^{3+} in the **B** sites of one unit cell.	6.0 pt

Besides doping in black ceramic glaze, chromium-containing pigments are used in painting and printing due to the abundant color originating from chromium with different oxidation states, such as $+2$, $+3$ and $+6$. The pigment, chrome green (Cr_2O_3) can be converted into a series of other compounds (**D-G**) in the following process, where **E**, **F**, **G** are yellow, orange and red respectively.

$$Cr_2O_3 \xrightarrow{\text{NaOH(aq)}} D \xrightarrow{H_2O_2} E \xrightarrow{H^+} F \xrightarrow{98\% \ H_2SO_4} G$$
green, yellow, orange, red

$$F \xrightarrow{H} Cr^{3+}$$
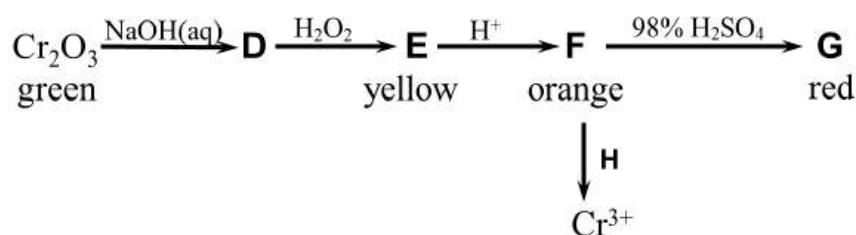
2.4	**Write** the chemical formula of **E**.	1.0 pt

2.5	**Write** the reaction equation of **F** $\longrightarrow$ **G**.	2.0 pt

2.6	**Choose** the agent which could be **H**. (A) $FeSO_4$ (B) $FeCl_3$ (C) $ZnSO_4$ (D) $CuSO_4$	1.0 pt

Theory

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Q2-4
English (Official)

The variable valence of chromium is not only important for the production of pigments, but also useful for catalysis. For example, a typical Phillips catalyst for the polymerization of ethylene consists of chromium oxide species grafted onto a porous support material such as amorphous silica. The tetra-coordinated $Cr(VI)$ specie is the core in the pre-catalyst (**1**), which is proposed to be reduced quickly into a six-coordinated $Cr(II)$ specie (**2**) by the ethylene molecules at the beginning. **2** is proposed to further catalyze polymerization of ethylene molecules.

2.7	The reaction of **1** with ethylene can be traced by UV–vis spectra, which show the light absorption of **1** at $21500\,cm^{-1}$ and the light absorption of **2** at $16700\,cm^{-1}$ in the visible region, respectively. **Choose** the appropriate combination of colors of **1** and **2**. (A) orange and white, respectively (B) orange and blue, respectively (C) blue and orange, respectively (D) blue and white, respectively	1.0 pt

2.8	Assuming that the $Cr(II)$ ion in **2** is located in a regular octahedral crystal field with a splitting energy Δ_o of $16000\,cm^{-1}$, **draw** the configurations of d electrons of the $Cr(II)$ ion in **2**, and **calculate** the crystal field stabilization energy (CFSE) for the $Cr(II)$ ion in **2**. (Note: The pairing energy P for $Cr(II)$ in **2** is $23500\,cm^{-1}$)	5.0 pt

2.9	Coordination compounds/ions exhibit paramagnetism when containing unpaired electrons, and the corresponding magnetic moment (μ) of transition metal cations is calculated by the function $\mu = \sqrt{n(n+2)}\,\mu_B$ where n is the number of unpaired electrons. **Calculate** the magnetic moment in term of μ_B for the $Cr(II)$ ion in **2**.	2.0 pt

Chromium in Ancient and Modern Times

11% of the total									
Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	**Total**
Points	2	1	6	1	2	1	1	5	2	**21**
Score										

2.1 (2.0 pt)

A : _____   **B** : _____

2.2 (1.0 pt)

2.3 (6.0 pt)

2.4 (1.0 pt)

2.5 (2.0 pt)

2.6 (1.0 pt)
[   ] (A)   [   ] (B)   [   ] (C)   [   ] (D)

2.7 (1.0 pt)
[   ] (A)   [   ] (B)   [   ] (C)   [   ] (D)

Theory

A2-3

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2.8 (5.0 pt)

CFSE = _____ cm^{-1}

2.9 (2.0 pt)

$\mu = $ _____ μ_{B}

Theory

Q3-1

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Capture and Transformation of Carbon Dioxide

Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10	3.11	3.12	**Total**
Points	2	5	2	3	2	8	2	2	5	7	2	2	**42**
Score													

Climate change is one of the most critical global challenges nowadays. The increase of CO_2 concentration in the atmosphere has been recognized as the primary driver of global warming. The study of the capture and transformation of CO_2 has attracted considerable attention.

Direct air capture (DAC) technology which aims to extract CO_2 directly from ambient air is promising. The conventional method of DAC is wet scrubbing with alkaline hydroxide solutions (typically NaOH), where CO_2 in air is absorbed till pH ≈ 10 (**step 1**). The spent sorbent is regenerated by dosing calcium hydroxide into the system (**step 2**). The white precipitate **A** received in **step 2** decomposes at 700 °C, giving rise to CO_2 and another white compound **B** (**step 3**). Finally, calcium hydroxide can be generated by the hydration of **B**. This process is highly energy-demanding. ($H_2CO_3 : K_{a1} = 4.5 \times 10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$)

3.1	**Write** the formulas for **A** and **B** respectively.	2.0 pt

3.2	**Write** the balanced equations of all possible reactions in **steps 1-3**. NaOH solution is used as sorbent.	5.0 pt

Recently, an electrochemical process was developed for regenerating the alkaline solution in the wet scrubbing process for DAC application, and pure CO_2 gas could be recovered that is suitable for storage or utilization. The process is based on a H_2-recycling electrochemical system (HRES), as shown in **Figure 3.1**.

Theory

Q3-2

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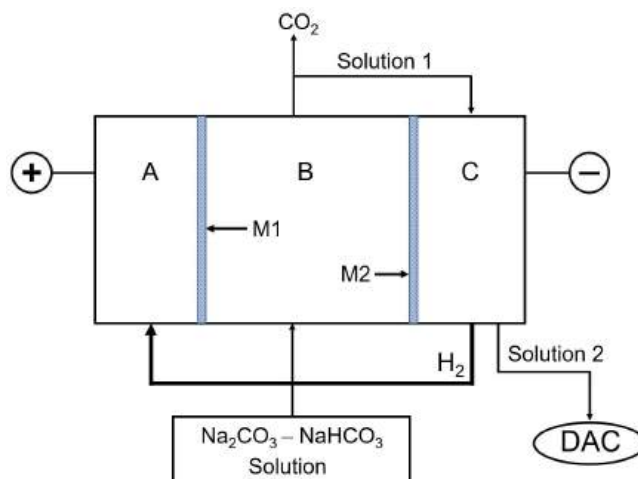
Figure 3.1 Schematic drawing of the experimental setup

The electrochemical cell contains three compartments: an anode region (A), an acidifying region (B), and a cathode region (C). They are separated by ion-selective permeable membranes M1 and M2. During the operation, protons produced from H_2 oxidation at the anode are transported to the acidifying compartment where the spent solution (Na_2CO_3-$NaHCO_3$) coming from the air contactor is fed. The decreasing pH of the solution leads to the conversions of carbonate to hydrocarbonate (**reaction 1**) and hydrocarbonate to carbonic acid (**reaction 2**). When the solution is saturated by dissolved CO_2 (solubility: $0.033\,mol\,L^{-1}$), a further pH decrease leads to the release of CO_2 gas (**reaction 3**). H_2 generated in the cathode is introduced to the anode and the solution from the cathode can be reused as a DAC absorbent.

3.3	**Write** the electrode reactions in the anode (A) and the cathode (C) respectively.	2.0 pt

3.4	**Write** the balanced equations for the reactions **1–3** in the acidifying region (B).	3.0 pt

3.5	**Check** all that correctly describe the movement of cations during the system operation. (a) H^+ ions permeate through M1 from A to B. (b) H^+ ions permeate through M2 from B to C. (c) Na^+ ions permeate through M1 from B to A. (d) Na^+ ions permeate through M2 from B to C. (e) Both H^+ and Na^+ ions can permeate through M1and M2.	2.0 pt

The cell works at a steady state when the current passing through the cell is 2.00 A and the flow rate of the solution ($0.050\,mol\,L^{-1}$ Na_2CO_3 - $0.10\,mol\,L^{-1}$ $NaHCO_3$) into the region B is $10.0\,mL\,min^{-1}$. The pH in the anode compartment is maintained at 1 in the steady state.

3.6	**Calculate** the generation rate of CO_2 gas (in $mmol\,min^{-1}$).	8.0 pt

Zeolitic imidazolate frameworks (ZIFs), a sub-class of metal–organic frameworks (MOFs) are promising

Theory

Q3-3

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materials for the capture and utilization of CO_2. The structures of ZIFs resemble zeolites. They form 3D frameworks with tetrahedrally coordinated metal ions (e.g. Zn^{2+}, Co^{2+}) bridged by imidazolate (Im^-) and its derivatives. As the conjugated base of imidazole (HIm), imidazolate anion binds to metal cations (M) by its two N atoms. The fact that the M-Im-M angle is similar to the Si-O-Si angle (145°) preferred in zeolites (as shown below) has led to the synthesis of a large number of ZIFs with zeolite-type tetrahedral topologies.
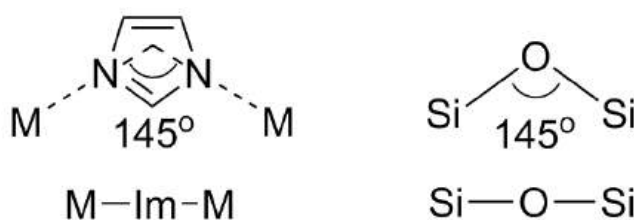
ZIF-8 is one of the representative ZIFs, which adopts a sodalite framework (**SOD**), as shown in **Figure 3.2**. ZIF-8 was firstly synthesized by Chinese scientists Xiao-Ming Chen et al. (they named it as MAF-4) by the reaction of Zn^{2+} with 2-methylimidazole ($CH_3(C_3N_2H_3)$, HmIm). It crystalizes in the cubic system with the cell parameter $a = 1.632$ nm for a solvent-free phase with the effective pore diameter (shown by the inside virtual sphere in **Figure 3.2d**) of 1.16 nm.

Theory

Q3-4

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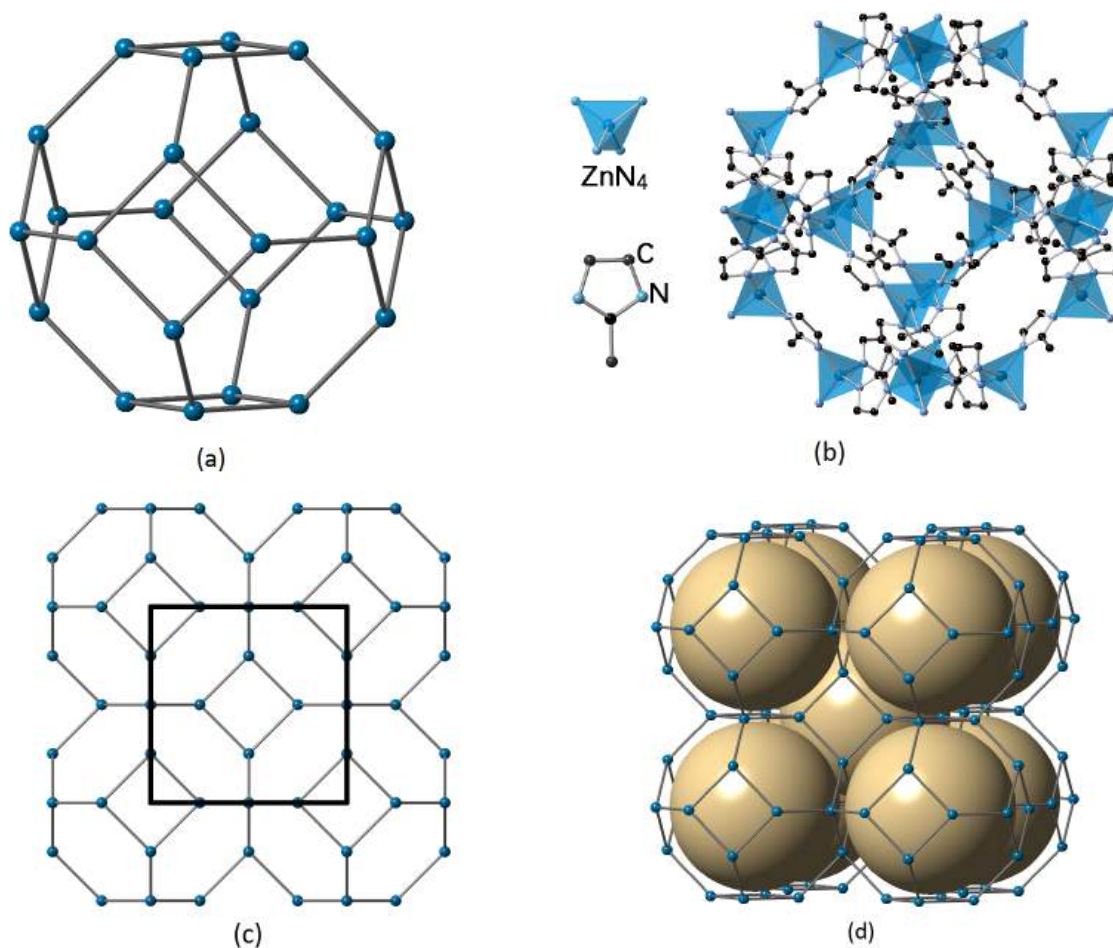
Figure 3.2 Topology of **SOD** and structure of ZIF-8

(a)   Topology of **SOD** cage;

(b)   **SOD** cage in ZIF-8 formed by Zn^{2+} (at the centers of the tetrahedra) and imidazolate (H atoms are omitted for clarity);

(c)   Framework of **SOD** with the unit cell shown by the square box;

(d)   Some of the pores are highlighted by virtual spheres in ZIF-8.

Note: If you wish, you may use the symbol "HmIm" and "mIm" representing 2-methylimidazole and 2-methylimidazolate respectively in solving the following questions.

3.7	**Write** the formula of the single sodalite cage.	2.0 pt

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3.8	**Write** the composition of the unit cell of ZIF-8.	2.0 pt

3.9	**Calculate** the inner surface area (S) of the pores (modeled by the virtual spheres) of 1 g ZIF-8 (in m^2). If you failed to get the composition of the unit cell, use 3500 as the formula weight of the unit cell.	5.0 pt

3.10	**Calculate** the porosity R of ZIF-8 (R is the ratio of pore volume to the actual volume of the material) and the pore volume of 1 g ZIF-8 (V_p, in cm^3).	7.0 pt

ZIF-8 can also act as a catalyst to promote the conversion of CO_2 to high value-added chemicals. One of the most promising routes for CO_2 fixation is the preparation of cyclic carbonates *via* CO_2 cycloaddition. An example is shown as below:
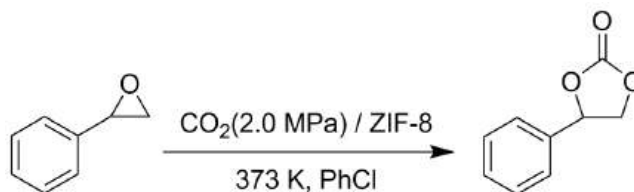
A mechanism of catalytic conversion of CO_2 to cyclic carbonate over ZIF-8 catalyst is proposed:
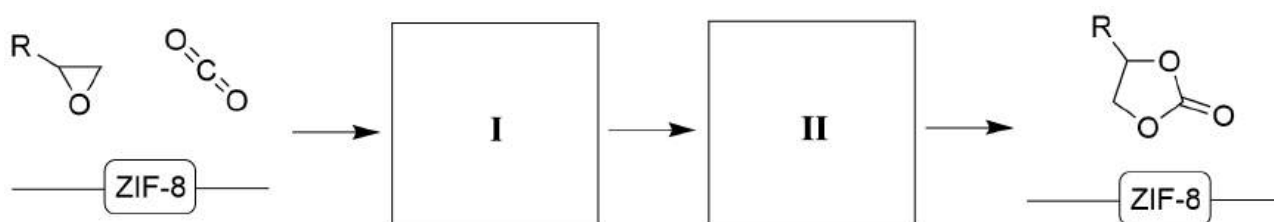
3.11 If ZIF-8 provides acid sites in the above catalytic process, complete the mechanism by choosing the reasonable intermediates from the following species: 2.0 pt

(a) (b) (c) (d)
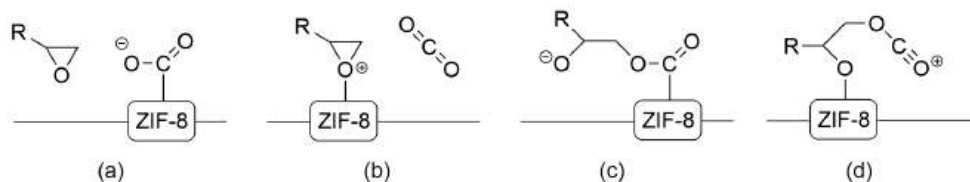
Choose the intermediates corresponding to **I** and **II** respectively.

ZIF-8 shows a relatively high thermal stability. However, a recent study revealed that its structure would be destroyed if applied in a wet acidic environment. The co-existence of CO_2 and H_2O with ZIF-8 resulted in the formation of $ZnCO_3$.

3.12 **Write** the balanced equation of ZIF-8 with CO_2 and H_2O. 2.0 pt

Capture and Transformation of Carbon Dioxide

14% of the total												
Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10	3.11	3.12	**Total**
Points	2	5	2	3	2	8	2	2	5	7	2	2	**42**
Score													

3.1 (2.0 pt)

A: _____   **B**: _____

3.2 (5.0 pt)

step 1:

step 2:

step 3:

Theory

A3-2

English (Official)

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3.3 (2.0 pt)

A:

C:

3.4 (3.0 pt)

reaction 1:

reaction 2:

reaction 3:

3.5 (2.0 pt)

[   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)   [   ] (e)

3.6 (8.0 pt)

$r(CO_2) = $ _____ $mmol\,min^{-1}$

3.7 (2.0 pt)

3.8 (2.0 pt)

3.9 (5.0 pt)

$S =$ _____m^2

3.10 (7.0 pt)

$R =$ _____; $V_p =$ _____cm^3

3.11 (2.0 pt)
I: [   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)
II: [   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)

3.12 (2.0 pt)

Theory

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Q4-1

English (Official)

A New Journey for Ancient Sulfur

16% of the total												
Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9	4.10	4.11	4.12	**Total**
Points	2	4	4	3	1	5	2	4	5	4	6	5	**45**
Score													
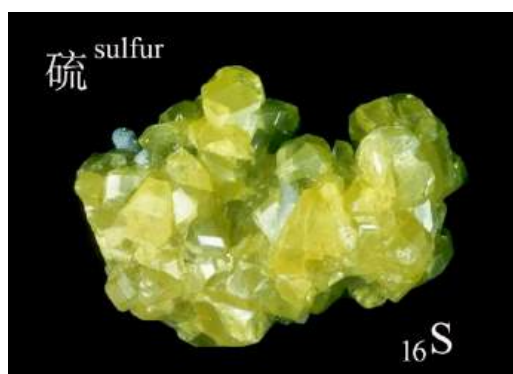
Sulfur has been known and used since the ancient times. Nowadays, sulfur is widely used in chemical production and pharmaceutical industry as an inexpensive chemical raw material.

Pyrite (FeS_2) is commonly used as a raw material in the industrial production of elemental sulfur. By heating pyrite in the presence of limited air supply, the theoretical yield of elemental sulfur is 100% and a black magnetic oxide (Fe_3O_4) is the other product.

4.1 **Write** the balanced reaction equation that describes the above conversion. 2.0 pt

---

In addition to sulfur, a small amount of SO_2 is generated as a by-product during the actual process. This reaction can be monitored by measuring the amount of SO_2. The following recipe is used for the monitoring:

Raw ore powder is heated in a temperature-controlled tube furnace. The generated SO_2 is absorbed by $2\ mol\ L^{-1}$ NaOH solution. When the reaction is completed, the solution is transferred to a 500 mL volumetric flask and diluted by distilled water to the mark. 25.00 mL of this diluted solution is then added into an iodine flask containing 50.00 mL $0.05122\ mol\ L^{-1}$ I_2 standard solution and 5 mL 20% H_2SO_4 solution. After maintaining the iodine flask in dark for 5 min, the solution is titrated with $0.1012\ mol\ L^{-1}$ $Na_2S_2O_3$

Theory

Q4-2

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standard solution. When the color of the solution turns light brown, 3 mL 0.5% starch indicator is added. Continue the titration until the blue color disappears.

4.2	**Write** the balanced reaction equations involving I_2 in the above measurement.	4.0 pt

4.3	In such a test experiment starting from pyrite, 17.6 g of elemental sulfur was collected. The analysis of the by-product gases according to the above procedure resulted in the consumption of 18.47 mL of $Na_2S_2O_3$ standard solution. Assuming that no other sulfur containing species were produced, **calculate** what percentage of the sulfur in pyrite was lost as the by-product?	4.0 pt

The lithium-sulfur battery is a compelling energy storage system because its high theoretical energy density exceeds conventional Li-ion batteries. The net reaction of a lithium-sulfur battery can be simplified as: $16\,Li + S_8 \longrightarrow 8\,Li_2S$. Sulfur is the cathode and metallic lithium is the anode active material during discharge.

4.4	**Write** the balanced equations for reactions that take place at cathode (**a**) and anode (**b**) during discharge.	3.0 pt

|		
4.5	**Calculate** the mass ratio of the cathode active material to the anode active material, according to the net battery reaction.	1.0 pt

A lithium-ion battery (LIB) that possesses an average operating voltage of 3.8 V and a deliverable capacity of 3110 mAh can provide energy for a mobile phone to play videos continuously for 22 hours upon a full charge.

4.6	If the LIB is replaced by an ideal lithium-sulfur battery pack, which has an average operating voltage of 4.2 V and contains 23 g sulfur as the active electrode material that can react stoichiometrically during discharge, **calculate** how many hours the new battery pack will provide energy for the phone to play videos continuously after a full charge.	5.0 pt

Elemental sulfur generally exist as S_8 molecules. In real lithium-sulfur batteries, S_8 is not directly reduced to Li_2S during discharge, but it undergoes stepwise reactions generating different soluble lithium polysulfides (Li_2S_n, $n = 3 - 8$). These lithium polysulfides could diffuse to the anode and corrode it, which results in the loss of active electrode materials. This phenomenon is called "shuttle effect".

4.7	**Write** the balanced reaction equation for the corrosion of anode by soluble lithium polysulfides (Li_2S_n) that produces Li_2S.	2.0 pt

In order to suppress the "shuttle effect", the forms of polysulfides in an electrolyte have been extensively studied. Li_2S_6 is one of the most representative intermediate products:

$$2Li^+ + S_8 + 2e^- \longrightarrow Li_2S_6 + 2S$$
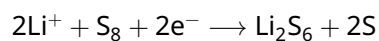
A theoretical study shows that two conformers with comparable energies, $Li_2S_6(I)$ and $Li_2S_6(II)$ coexist in 1,2-dimethoxyethane (DME), a common electrolyte solvent in lithium-sulfur batteries. The dissociation of Li_2S_6 in DME is shown below:
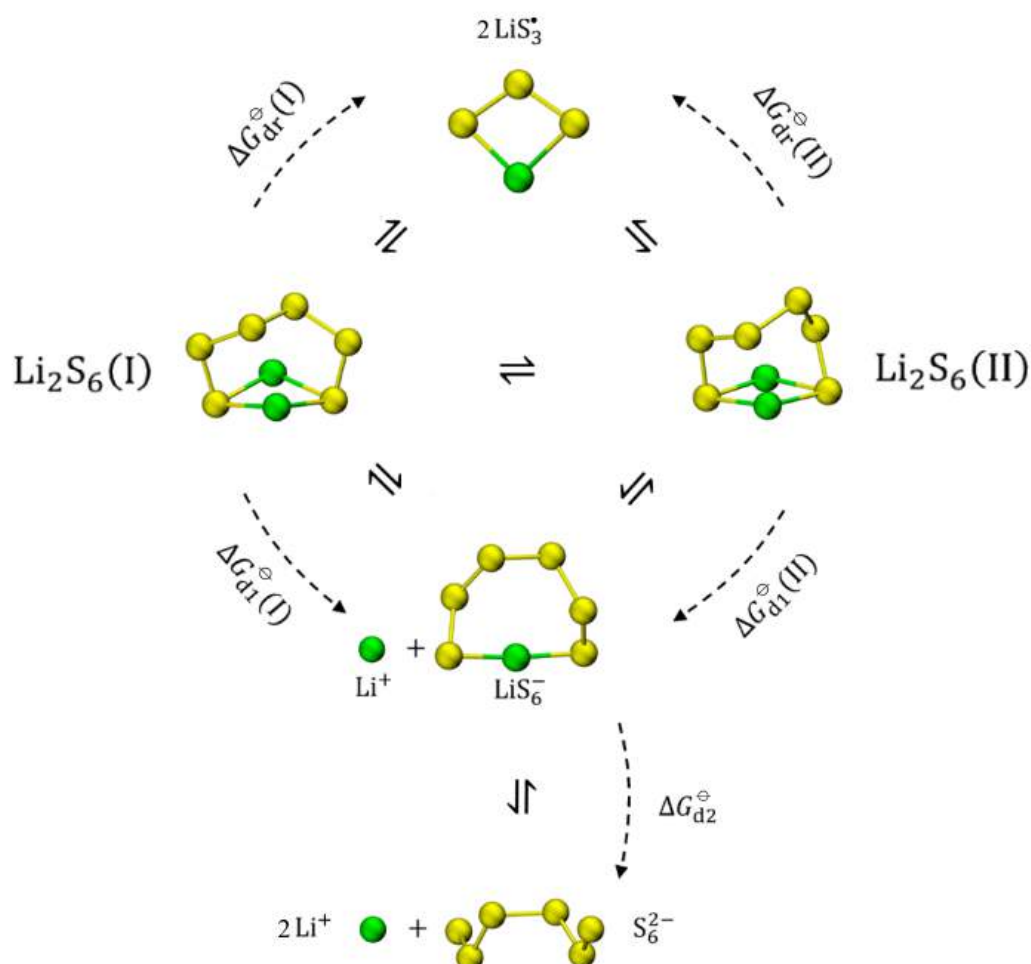
Chemical equilibria of Li_2S_6, LiS_6^-, S_6^{2-} and $LiS_3^\bullet$ in DME

Table 4.1 Dissociation Gibbs energies (kJ mol^{-1}) of different reactions in DME (298.15 K, 1 bar)

$\Delta G_{d1}^{\ominus}(I)$	$\Delta G_{d1}^{\ominus}(II)$	$\Delta G_{d2}^{\ominus}$	$\Delta G_{dr}^{\ominus}(I)$	$\Delta G_{dr}^{\ominus}(II)$
20.68	18.92	100.55	45.13	43.37

4.8	Using the data from **Table 4.1**, <u>**calculate**</u> the equilibrium concentration ratio of two conformers in DME (298.15 K, 1 bar), $\dfrac{[Li_2S_6(II)]}{[Li_2S_6(I)]}$.	4.0 pt

4.9	Using the data from **Table 4.1**, <u>**calculate**</u> the apparent dissociation constant of $Li_2S_6 \longrightarrow Li^+ + LiS_6^-$ in DME (298.15 K, 1 bar).	5.0 pt

4.10	<u>**Sort**</u> the following equilibrium concentrations in decreasing order: $[Li_2S_6]$, $[LiS_6^-]$, $[S_6^{2-}]$, $[LiS_3^{\bullet}]$ in DME.	4.0 pt

4.11	The standard reduction potential of metallic lithium in water at 298.15 K and 1 bar is: $$E^{\ominus}\left(Li^+/Li\right) = -3.040 \text{ V}$$ The standard solvation Gibbs energies of gaseous $Li^+(g)$ to $Li^+(sol)$ in different solvents.	6.0 pt

	$Li^+(H_2O)$	$Li^+(DME)$
$\Delta G^{\ominus}/\text{kJ mol}^{-1}$	-116.9	-114.6

<u>**Calculate**</u> the standard reduction potential of metallic lithium electrode in DME.

Studies have shown that electromotive force of a lithium-sulfur battery would be increased by replacing DME with dimethyl sulfoxide (DMSO). Therefore, the forms of polysulfides in DMSO also attract researchers' attention.

In a test, a certain amount of Li_2S and 4.81 mg sulfur powder were added into 10.00 mL DMSO, then heated and stirred until completely dissolved (ignoring the change in volume). Suppose that only the following polysulfides were present in the DMSO: $S_3^{\bullet-}$, S_4^{2-}, S_5^{2-}, S_6^{2-}, S_7^{2-}, S_8^{2-}. The equilibrium concentration ratio of the sulfur containing species was:

$$[S_3^{\bullet-}] : [S_4^{2-}] : [S_5^{2-}] : [S_6^{2-}] : [S_7^{2-}] : [S_8^{2-}] = 17.50 : 1.00 : 4.50 : 55.00 : 5.00 : 0.75$$

4.12	<u>**Calculate**</u> the original mass m (in mg) of Li_2S added to DMSO.	5.0 pt

A New Journey for Ancient Sulfur

16% of the total												
Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9	4.10	4.11	4.12	**Total**
Points	2	4	4	3	1	5	2	4	5	4	6	5	**45**
Score													

4.1 (2.0 pt)

4.2 (4.0 pt)

4.3 (4.0 pt)

_____%

4.4 (3.0 pt)

   (a)

   (b)

4.5 (1.0 pt)

mass ratio:_____

4.6 (5.0 pt)

_____h

4.7 (2.0 pt)

4.8 (4.0 pt)

$$\frac{[\mathsf{Li}_2\mathsf{S}_6(\mathrm{II})]}{[\mathsf{Li}_2\mathsf{S}_6(\mathrm{I})]} = \underline{\hspace{6cm}}$$

4.9 (5.0 pt)

$K_{d1}^{\ominus} =$ _____
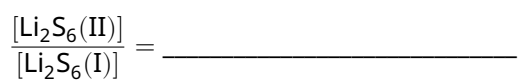
4.10 (4.0 pt)

(1)_____ > (2)_____ > (3)_____ > (4)_____

4.11 (6.0 pt)

$E^{\ominus}(\text{Li}^+(\text{DME})/\text{Li}) = \underline{\hspace{6cm}}\text{V}$

4.12 (5.0 pt)

$m(\text{Li}_2\text{S}) = \underline{\hspace{5cm}}\text{mg}$

Interconversion among Nitrogen Oxides

15% of the total										
Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	5.10	**Total**
Points	4	4	2	4	3	8	4	6	4	6	**45**
Score											

Nitrogen oxides (including N_2O, NO, NO_2, N_2O_4 and etc., usually written as NO_x) are one of the main air pollutants that can cause a series of problems such as ozone depletion, acid rain, photochemical smog, and greenhouse effect. Therefore, the emission and conversion of NO_x must be controlled to improve air quality. Here let us investigate the oxidation of NO to NO_2 *via* the reaction of $2NO + O_2 \longrightarrow 2NO_2$.

Part A

It is generally accepted that this reaction proceeds through the following mechanism in the atmosphere:

$$2\,NO \rightleftharpoons N_2O_2 \tag{1}$$

$$N_2O_2 + O_2 \longrightarrow 2\,NO_2 \tag{2}$$

Reaction (1) and (2) and the reverse of reaction (1) are elementary reactions. Reaction (1) is a pre-equilibrium reaction, and its equilibrium constant in terms of concentrations is denoted as K_{c1}. Reaction (2) is the rate-determining step of the overall reaction, and its rate constant is k_2.

5.1	**Deduce** the rate expression for the overall reaction of $2NO + O_2 \longrightarrow 2NO_2$ as a function of [NO], [O_2], K_{c1} and k_2.	4.0 pt

The temperature dependence of K_{c1} could be approximately described as $\ln K_{c1} = M - (N/T)$ (M and N are constants). The change of k_2 with temperature follows the Arrhenius equation with the pre-exponential factor of A_2 and apparent activation energy of $E_{a,2}$. Assume that $E_{a,2}$ and A_2 are independent of the temperature.

5.2	**Deduce** the expressions for the pre-exponential factor (A_+) and apparent activation energy (E_{a^+}) of the reaction of $2NO + O_2 \longrightarrow 2NO_2$ as functions of M, N, A_2 and $E_{a,2}$.	4.0 pt

Theory

Q5-2

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The apparent rate constant (k_+) of the overall reaction is $6.63 \times 10^5 \, \text{L}^2 \, \text{mol}^{-2} \, \text{min}^{-1}$ at 600 K, and its apparent activation energy is $1.20 \, \text{kJ} \, \text{mol}^{-1}$.

5.3	**Calculate** the rate constant (in $\text{L}^2 \, \text{mol}^{-2} \, \text{min}^{-1}$) of this reaction at 700 K.	2.0 pt

The standard enthalpies of formation ($\Delta_f H_m^\ominus$) and standard entropies ($S_m^\ominus$) at 298.15 K are as follows:

	NO(g)	O$_2$(g)	NO$_2$(g)
$\Delta_f H_m^\ominus$ (kJ mol^{-1})	91.3		33.1
$S_m^\ominus$ (J K^{-1} mol^{-1})	210.8	205.2	240.1

The standard reaction enthalpy and entropy changes of $2NO + O_2 \longrightarrow 2NO_2$ can be regarded as temperature independent. All the gases are taken to be ideal for the following questions.

5.4	**Calculate** the thermodynamic equilibrium constant ($K_p^\ominus$) of this reaction at 600 K.	4.0 pt

5.5	**Calculate** the standard internal energy change $\Delta_r U_m^\ominus$ (in kJ mol^{-1}) of this reaction at 600 K.	3.0 pt

Experimental observation shows that the rate of the reaction of $2NO_2 \longrightarrow 2NO + O_2$ is independent on the concentration of NO and O$_2$.

5.6	**Deduce** the expression of the rate for this reaction (the apparent rate constant could be directly used as k_-) and **calculate** the value of k_- apparent at 600 K. (If you failed to find the $K_p^\ominus$ (600 K) in question **5.4**, use $K_p^\ominus$ (600 K) = 350.0)	8.0 pt

NO$_2$ gas is introduced to a container with a fixed volume which is held at 600 K and allowed to reach equilibrium. 20 percent of the reactant is converted to NO and O$_2$. All the gases are taken to be ideal.

5.7	**Calculate** the total pressure of this reaction system at equilibrium. (If you failed to find the $K_p^\ominus$(600 K) in question **5.4**, use $K_p^\ominus$(600 K) = 350.0)	4.0 pt

Part B

Industrial exhaust is a main source of NO$_x$. One of the approaches to reduce the emission of NO$_x$ is through the oxidation of NO to NO$_2$ and the subsequent absorption of the formed NO$_2$ by absorbents. However, because of the low concentration of NO in exhaust, its spontaneous oxidation in the atmosphere is too slow to meet the demand of industry. Generally, solid catalysts are used to accelerate this reaction. The NO oxidation proceeds on the surface of a specific catalyst (**CatX**) through the following mechanism (adsorption site is denoted as Site):

$$O_2(g) + 2\,Site \underset{k_{S-1}}{\overset{k_{S+1}}{\rightleftharpoons}} 2\,O\text{-Site} \tag{S1}$$

$$r_{S+1} = k_{S+1}\,[O_2]\,\theta_v^2 \qquad r_{S-1} = k_{S-1}\theta_O^2$$

$$NO(g) + Site \underset{k_{S-2}}{\overset{k_{S+2}}{\rightleftharpoons}} NO\text{-Site} \tag{S2}$$

$$r_{S+2} = k_{S+2}[NO]\theta_v \qquad r_{S-2} = k_{S-2}\theta_{NO}$$

$$NO(g) + O\text{-Site} \xrightarrow{k_{S+3}} NO_2\text{-Site} \tag{S3}$$

$$r_{S+3} = k_{S+3}[NO]\theta_O$$

$$NO_2\text{-Site} \underset{k_{S-4}}{\overset{k_{S+4}}{\rightleftharpoons}} NO_2(g) + Site \tag{S4}$$

$$r_{S+4} = k_{S+4}\theta_{NO_2} \qquad r_{S-4} = k_{S-4}\,[NO_2]\,\theta_v$$

Assume that the adsorptions of NO, NO_2 and O (from the dissociation of O_2) cannot proceed beyond a monolayer coverage, and these species are adsorbed by the same kind of surface sites. Their fractional coverages (θ, defined as the ratio of the number of adsorption sites occupied to the number of total adsorption sites) are denoted as θ_{NO}, θ_{NO_2} and θ_O, respectively. Thus, the fraction of unoccupied adsorption sites (θ_v) is $\theta_v = 1 - \theta_{NO} - \theta_{NO_2} - \theta_O$. Assume that all the adsorption and desorption processes are much faster than reaction (S3).

5.8	**Deduce** the expression for θ_v as a function of $[NO]$, $[O_2]$, $[NO_2]$ and the rate constants involved in reactions (S1)–(S4).	6.0 pt

5.9   **Choose** the correct expression for the rate of $2\,NO\,(g) + O_2(g) \longrightarrow 2\,NO_2(g)$ at   4.0 pt
the beginning of the reaction. Assume that the concentration and adsorption
of NO_2 are both negligible.

(A) $r_{S+} = \dfrac{k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[NO][O_2]^{0.5}}{1 + (k_{S+1}[O_2]/k_{S-1})^{0.5} + k_{S+2}[NO]/k_{S-2}}$

(B) $r_{S+} = \dfrac{0.5k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[NO][O_2]^{0.5}}{1 + (k_{S+1}[O_2]/k_{S-1})^{0.5} + k_{S+2}[NO]/k_{S-2}}$

(C) $r_{S+} = \dfrac{k_{S+3}(k_{S+1}/k_{S-1})[NO][O_2]^{0.5}}{1 + k_{S+1}[O_2]/k_{S-1} + k_{S+2}[NO]/k_{S-2}}$

(D) $r_{S+} = \dfrac{k_{S+4}k_{S+3}(k_{S+1}/k_{S-1})^{0.5}[NO][O_2]^{0.5}/k_{S-4}}{1 + k_{S+1}([O_2]/k_{S-1})^{0.5} + k_{S+2}[NO]/k_{S-2}}$

For some catalysts, the surface reaction proceeds via an alternative way instead of reaction (S3):

$$NO\text{-Site} + O\text{-Site} \xrightarrow{k_{S+5}} Site + NO_2\text{-Site} \tag{S5}$$

$$r_{S+5} = k_{S+5}\theta_{NO}\theta_O$$

This step is also rate-determining for the overall reaction.

A catalyst (**CatY**) is used to promote the reaction of $2NO + O_2 \longrightarrow 2NO_2$. When the temperature and NO concentration are constant, the initial reaction rate changes with the concentration of O_2 as follows:

Theory

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Q5-5

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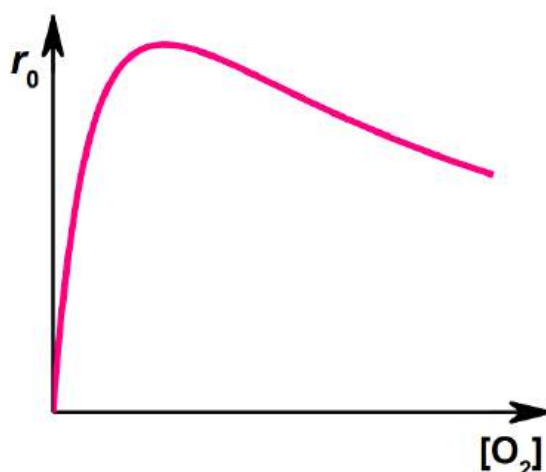
5.10	**Choose** a mechanism that is consistent with this curve. (A) S3 (B) S5 (C) cannot be determined	6.0 pt

Interconversion among Nitrogen Oxides

15% of the total										
Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	5.10	**Total**
Points	4	4	2	4	3	8	4	6	4	6	**45**
Score											

5.1 (4.0 pt)

$r_+ = $ _____

5.2 (4.0 pt)

$A_+ = $ _____, $E_{a^+} = $ _____

5.3 (2.0 pt)

$k_+(700\,\text{K}) = $ _____$\text{L}^2\,\text{mol}^{-2}\,\text{min}^{-1}$

5.4 (4.0 pt)

$K_p^{\ominus}(600\,\text{K}) = $ _____

5.5 (3.0 pt)

$\Delta_r U_m^{\ominus} = $ _____kJ mol^{-1}

5.6 (8.0 pt)

$r_- = $ _____, $k_-(600\,\text{K}) = $ _____

5.7 (4.0 pt)

p_total = _____kPa

5.8 (6.0 pt)

$\theta_{\mathrm{v}} = $ _____

5.9 (4.0 pt)
[   ] (A)   [   ] (B)   [   ] (C)   [   ] (D)

5.10 (6.0 pt)
[   ] (A)   [   ] (B)   [   ] (C)

Theory

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Q6-1

English (Official)

Enabling Phosphines

Phosphines are phosphorus analogues of amines. They also carry a lone pair of electrons at the phosphorus atom and thus exhibit Lewis basicity or nucleophilicity. But in contrast with tertiary amines, chiral phosphines like **P1** with three different substituents can be isolated as single enantiomers. Chiral phosphines are often used as chiral ligands in transition metal catalysis.

P1

$[\alpha]_D^{20} = +46$
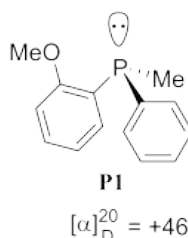
6.1 Using *R/S* symbol, **assign** the absolute configuration of **P1**. 3.0 pt

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In the past two decades, as organocatalysis grew rapidly, a large number of nucleophilic phosphine-catalyzed synthetic reactions have emerged. Among them, one of the most famous phosphine-catalyzed reactions is the Lu (3+2) cycloaddition reaction, which was first developed by Chinese scientist Xiyan Lu. For instance, under the catalysis of triphenylphosphine, ethyl allenoate **1** and methyl acrylate **2** smoothly produce two cyclopentene derivatives **3** (major) and **4** (minor).

Lu (3+2) cycloaddition:

Theory

Q6-2

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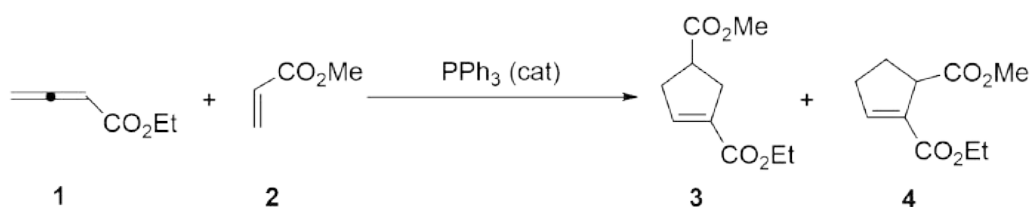
In a generally accepted mechanism, the Lu (3+2) reaction is a *formal* cycloaddition reaction. Initially, the catalyst triphenylphosphine engages in a nucleophilic addition to ethyl allenoate **1** to generate a zwitterionic intermediate **A**, which subsequently cyclizes with methyl acrylate **2** by two paths. In the path leading to compound **3**, an *in situ* generated phosphorus ylide intermediate **B** reversibly converts into intermediate **C** *via* proton transfer; **C** undergoes an elimination to deliver the major product **3** and release the phosphine catalyst. In the path leading to compound **4**, a phosphorus ylide intermediate **B'** is formed, which also reversibly converts into intermediate **C'** *via* proton transfer; **C'** undergoes an elimination to give the minor product **4** and regenerate the phosphine catalyst.

Mechanism:
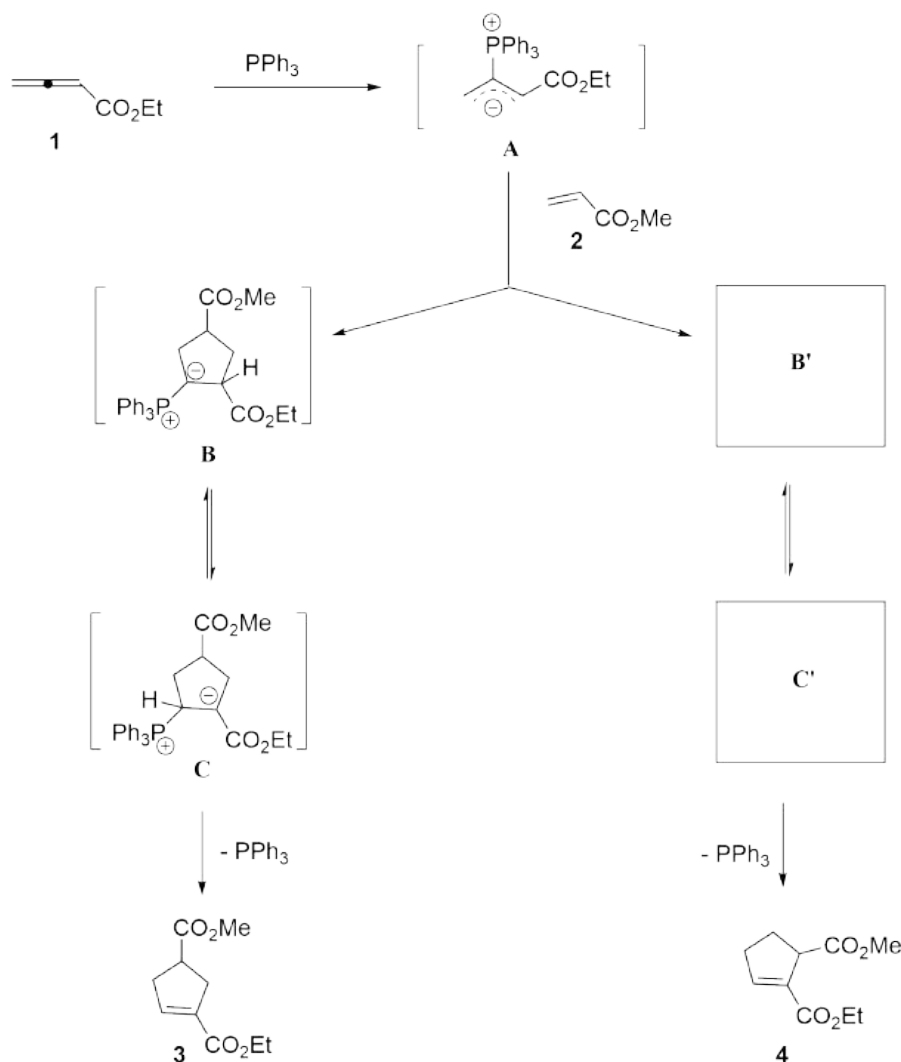
6.2	**Draw** the two **major** resonance structures that make up the shown resonance hybrid **A** (the involvement of ester group is not considered, and stereochemistry is not required).
	6.0 pt

Theory

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| 6.3	**Draw** the structures of intermediates **B'** and **C'** (stereochemistry is not required).	8.0 pt

Under similar conditions, ethyl allenoate **1** and diethyl fumarate **5** readily deliver the corresponding cycloaddition product **6**.
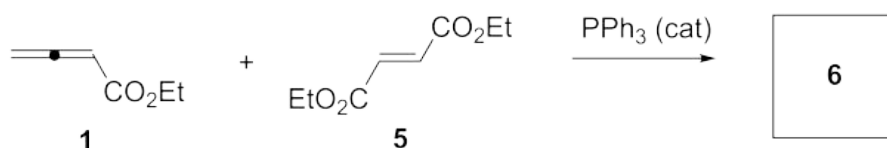
6.4	**Draw** the structure of compound **6** (stereochemistry is not required).	5.0 pt

Asymmetric Lu (3+2) cycloaddition reaction can be readily realized by utilizing chiral phosphine catalysts. For example, under the catalysis of a chiral bicyclic phosphine **P2**, ethyl allenoate **1** and methyl acrylate **2** smoothly delivered an enantio-enriched cycloaddition product **3** in 80% ee (enantiomeric excess).

Asymmetric Lu (3+2) cycloaddition:
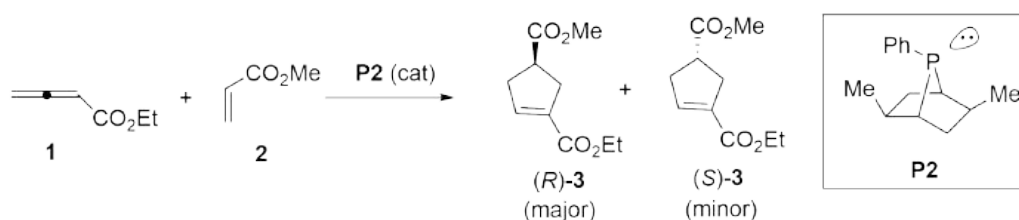
Calculation equation of ee:

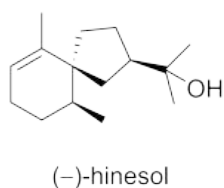$$\text{ee} = \frac{n_{\text{major}} - n_{\text{minor}}}{n_{\text{major}} + n_{\text{minor}}} \times 100\%$$

$n_{\text{major}} =$ the amount of major enantiomer

$n_{\text{minor}} =$ the amount of minor enantiomer

Theory

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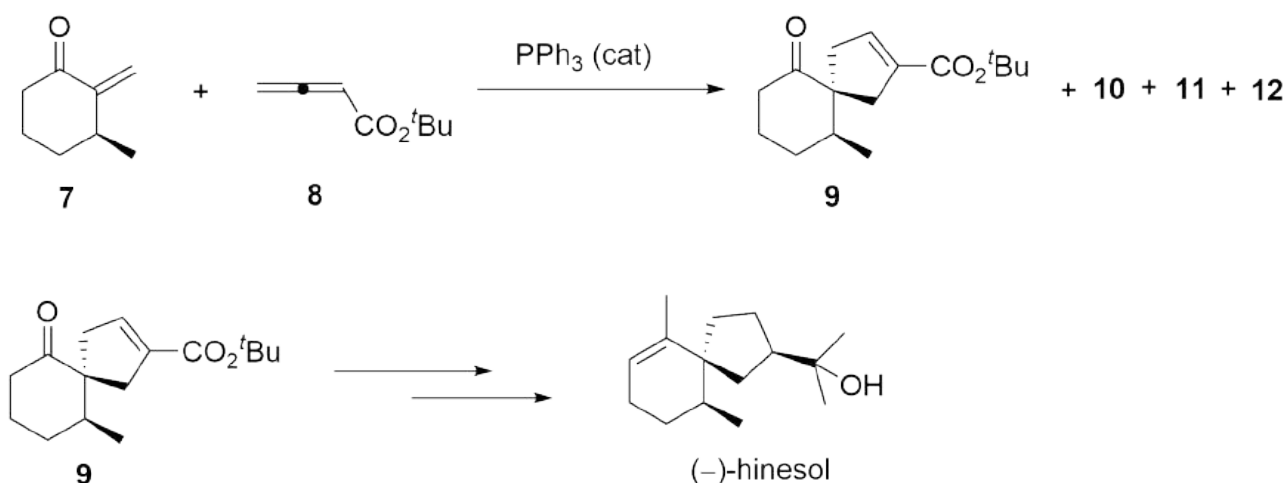TIANJIN, CHINA

Q6-4

English (Official)

6.5	**Mark** the chirality centers in the chiral phosphine **P2** by using asterisks. (**Note**: points will be deducted for every wrong asterisk until 0 points)	6.0 pt

6.6	**Give** the ratio of $n_{\text{major}}/n_{\text{minor}}$ of product **3**.	3.0 pt

Lu (3+2) cycloaddition reaction is a versatile tool in organic synthesis. For example, it was successfully used to synthesize (–)-hinesol, an important component of the Chinese medicinal herb Chang Zhu (*Atractylodes lancea var Chinensis*). Under the catalysis of PPh$_3$, a chiral cyclohexanone **7** cyclized with *tert*-butyl allenoate **8**, affording a major product **9** and three minor products **10**, **11** and **12**. Minor products **10**−**12** are all the isomers of **9**. Compound **9** could be readily transformed into (–)-hinesol by a multistep process.

(−)-hinesol

Chang Zhu

7 + 8 → PPh$_3$ (cat) → 9 + 10 + 11 + 12

9 → (−)-hinesol

Theory

Q6-5

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

6.7 In the following compounds, <u>**choose**</u> which one **does not** belong to the minor products **10**–**12**.   5.0 pt
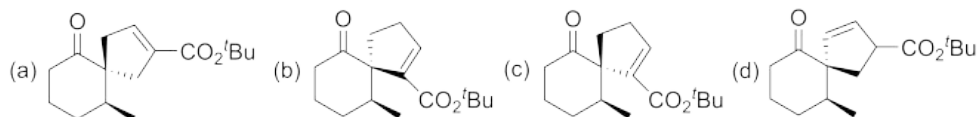
Enabling Phosphines

7% of the total							
Question	6.1	6.2	6.3	6.4	6.5	6.6	6.7	**Total**
Points	3	6	8	5	6	3	5	**36**
Score								

6.1 (3.0 pt)

_____

6.2 (6.0 pt)

6.3 (8.0 pt)

B' (4.0 pt)	**C'** (4.0 pt)

6.4 (5.0 pt)

6

6.5 (6.0 pt)

P2

6.6 (3.0 pt)

_____

6.7 (5.0 pt)
[   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)

Theory

54th IChO2022
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Q7-1

English (Official)
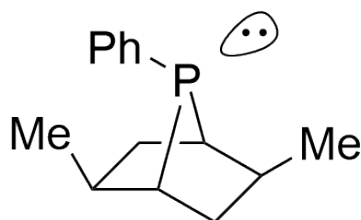
Organic Molecules in Life

9% of the total				
Question	7.1	7.2	7.3	**Total**
Points	12	8	12	**32**
Score				

The synthesis of complex peptides and proteins is a challenging task. On September 17, 1965, Chinese scientists synthesized crystalline bovine insulin artificially for the first time, marking a crucial step in the journey of exploring the secret of life and opening the era of protein synthesis.

Stamp issued on the 50th anniversary (2015) of the first synthesis of crystalline bovine insulin

Coupling of carboxylic acid groups with amine groups to forge an amide bond is the most elementary reaction in the synthesis of peptides and proteins. Allenone **2** was reported to be able to activate the carboxylic acid **1** under mild reaction conditions forming the intermediate **3**. Intermediate **3** then reacts with amine **4** to give amide **5** with high yield, along with the byproduct **6**.

Theory

Q7-2

54ᵗʰ IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)
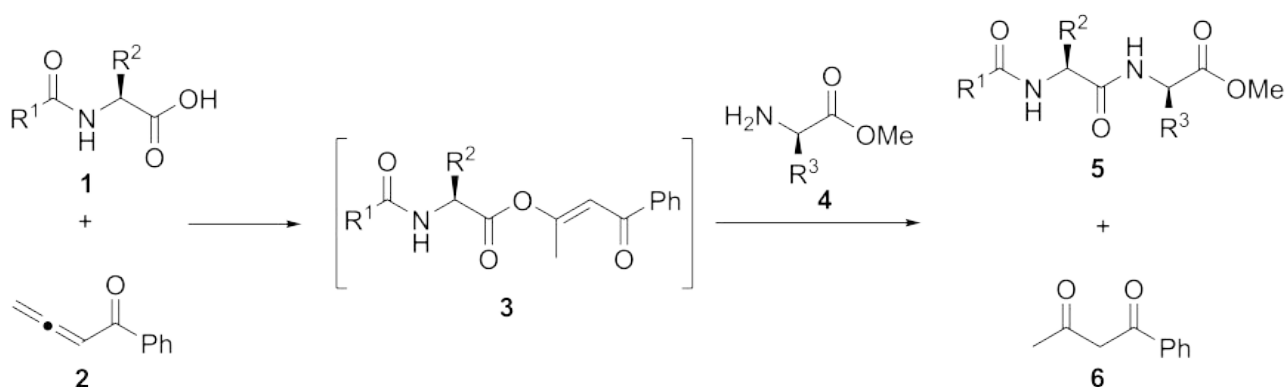
Similarly, *N*-ethynyl-*N*-methyl-*p*-toluenesulfonamide (MYTsA) with its major resonance structure **7** (involvement of Ts group is not considered) can activate carboxylic acid in the same way as allenone **2**.
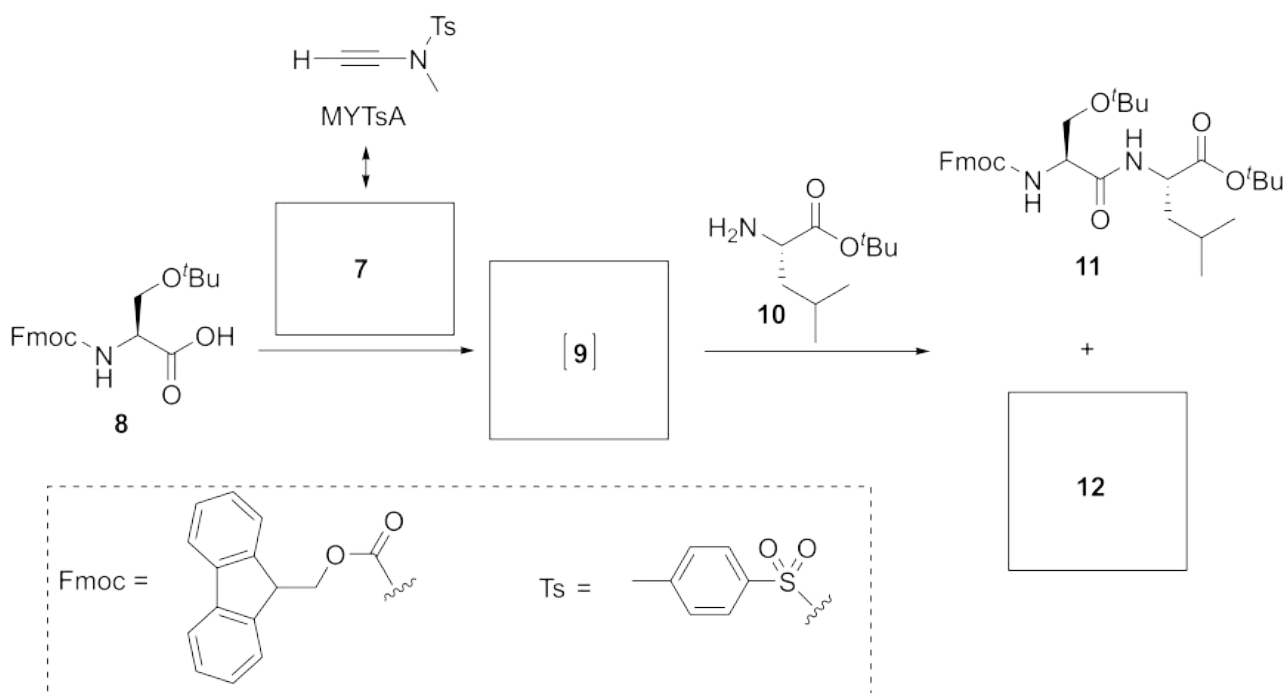
7.1	**Draw** the structures of **7**, intermediate **9** and compound **12**. Show the stereochemistry of any stereocenters.	12.0 pt

As the length of peptide chain grows, formation of amide bonds becomes more difficult, and conventional condensation methods are not applicable in the synthesis of proteins. In the first synthesis of crystalline bovine insulin, a method based on the chemistry of acylhydrazine **13** was developed to achieve the challenging amide coupling between two peptides. As the following equations, compound **15** reacts

with **16** smoothly in the presence of triethylamine.
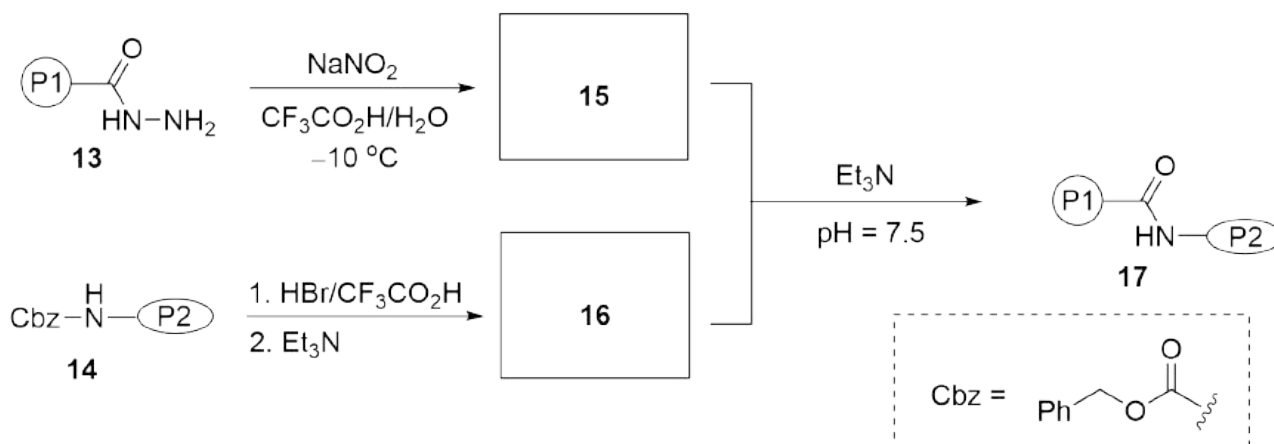

Note: P1, P2 = peptides

7.2	**Draw** the structures of compounds **15** and **16**.	8.0 pt

In addition to *de novo* synthesis, scientists can modify existing proteins. Although there are multiple reactive sites on the surface of protein, such as amino groups, thiol groups, and carboxyl groups, the most nucleophilic thiol groups are the preferred site when the protein is treated with electrophilic reagents such as *N*-phenyl maleimide **18** *via* Michael addition.
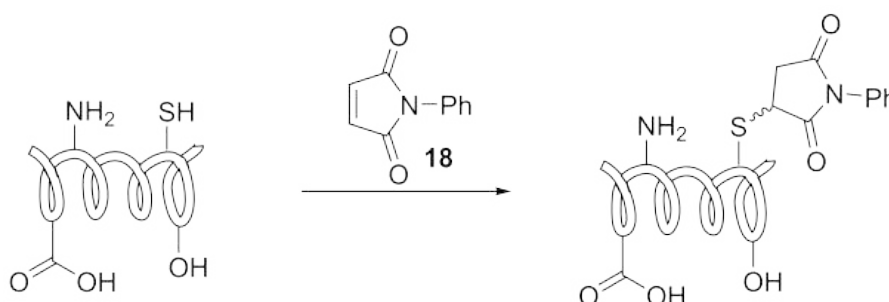
Under mild basic conditions (pH = 7.5), reagent **19** was proposed to react with the thiol group of protein **20** to give a neutral intermediate **21** which is attacked by hydroxide to give compound **22**. Compound **22** can equilibrate with an acyclic form **23**, and subsequently react with another protein **20**. The resulting major product can exist either in the acyclic form **24** or in the cyclic form **25** in a similar way as the equilibration between **22** and **23**.

Theory

Q7-4

54th IChO2022
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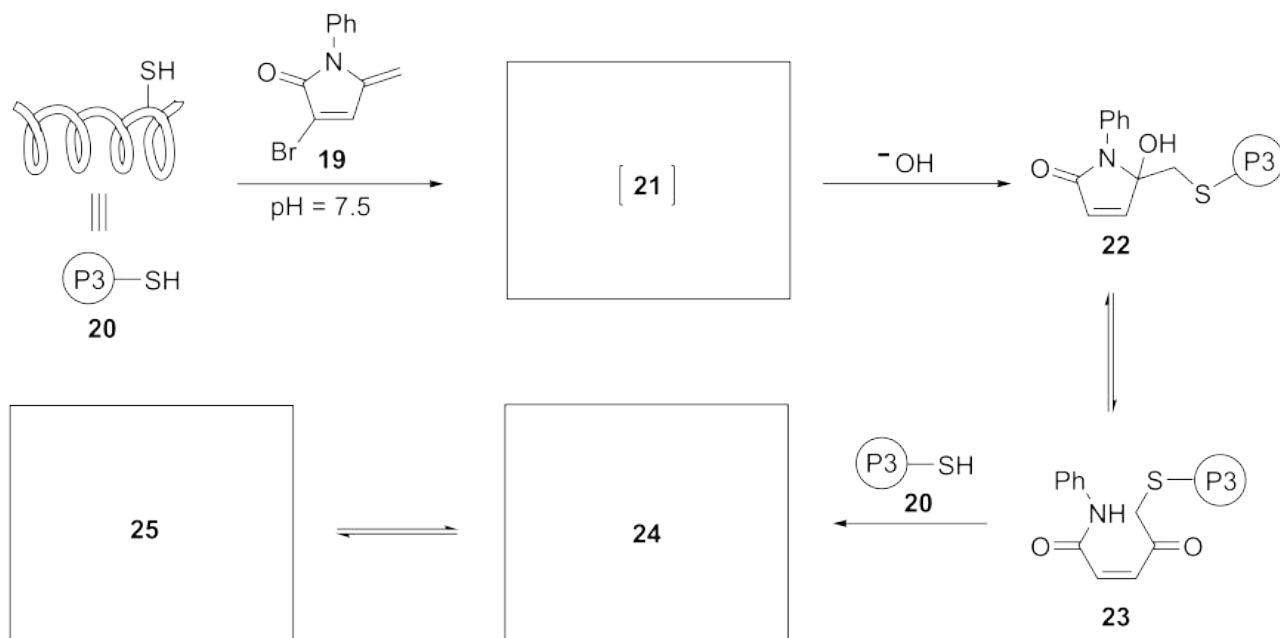
English (Official)

7.3 **Draw** the structures of intermediate **21**, compounds **24** and **25**. Stereochemistry is not required. | 12.0 pt

Theory

54ᵗʰ IChO2022
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TIANJIN, CHINA

A7-1
English (Official)

Organic Molecules in Life

7.1 (12.0 pt)

7 (4.0 pt)	**9** (4.0 pt)	**12** (4.0 pt)

7.2 (8.0 pt)

15 (4.0 pt)	**16** (4.0 pt)

7.3 (12.0 pt)

21 (4.0 pt)	**24** (4.0 pt)	**25** (4.0 pt)

Theory

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

Q8-1

English (Official)

Amazing Chiral Spiro Catalyst

10% of the total								
Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	**Total**
Points	16	2	2	2	2	8	2	2	**36**
Score									

Chiral compounds are important for human health, for example, more than 50% of the medicines currently in clinical use are single enantiomers of chiral molecules. However, synthesizing chiral molecules in enantio-enriched form is a great challenge. Professor Qilin Zhou's team in Nankai University in China developed a series of chiral spiro catalysts with high activity, raising the efficiency of asymmetric synthesis to a new height, and being widely used in the pharmaceutical industry. These catalysts can give up to (reach up to) 99.9% ee and can be used down to 0.00002 mol% loading. This research result won the first prize of the 2019 National Natural Science Award of China.
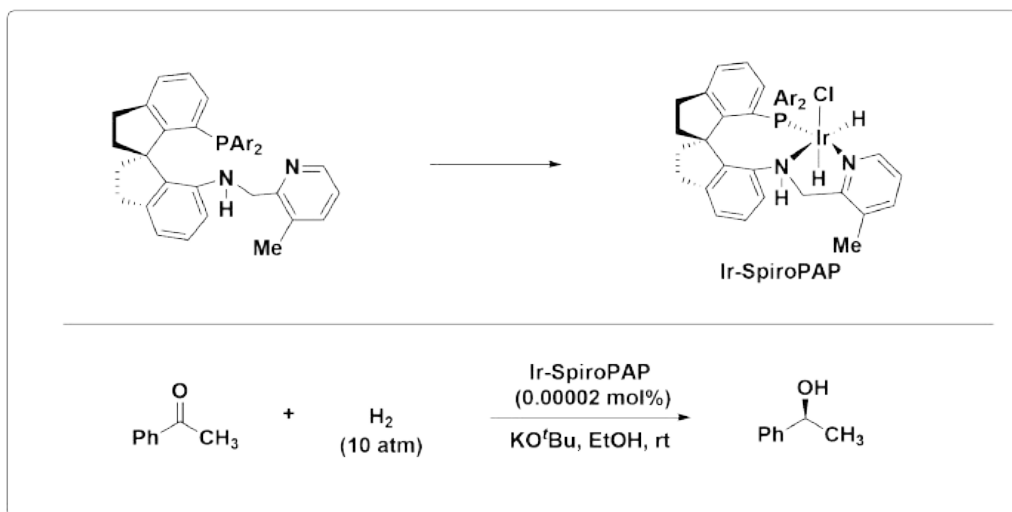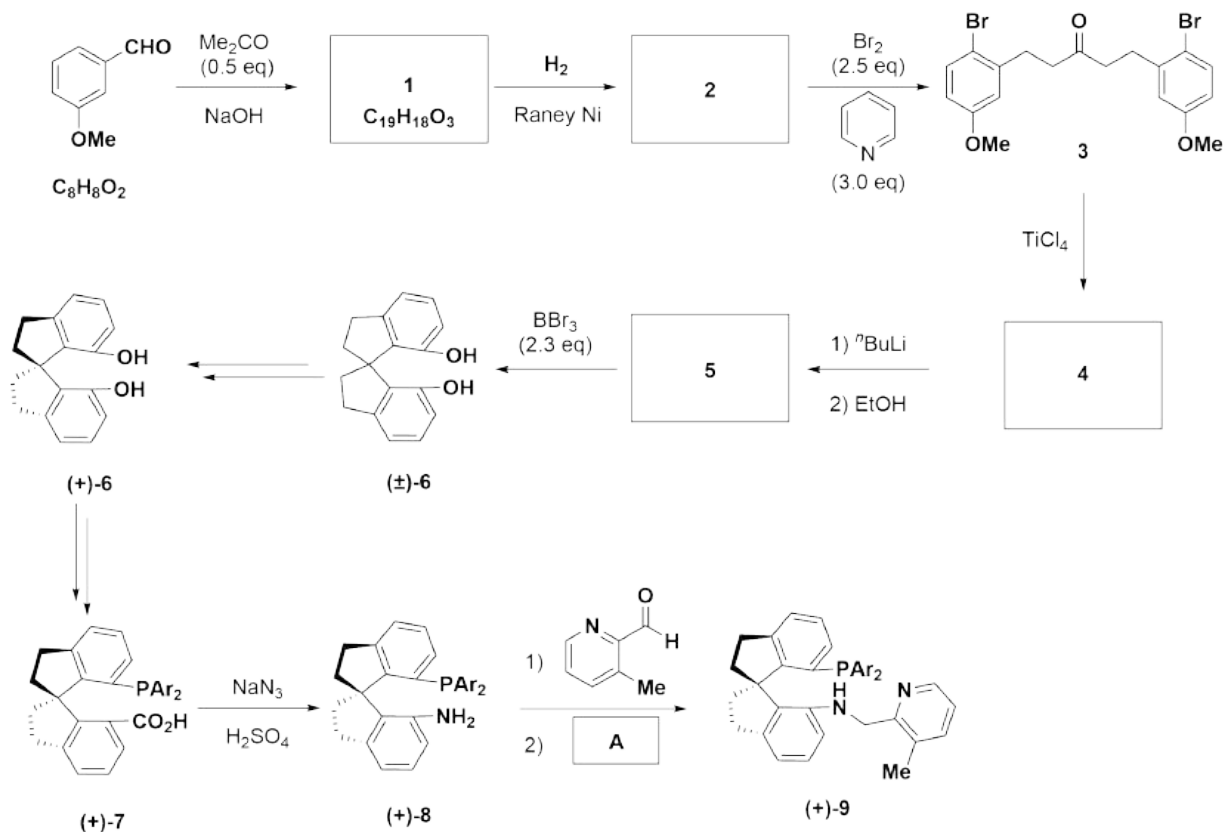

Note:
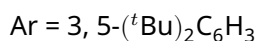
Ar = 3, 5-(^{t}Bu)$_2$C$_6$H$_3$

Part A

The synthetic route of the chiral ligand SpiroPAP is shown in the following scheme.

Theory

Q8-2

54ᵗʰ IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

Note:

eq = equivalent

Ar = 3, 5-(^{t}Bu)$_2$C$_6$H$_3$

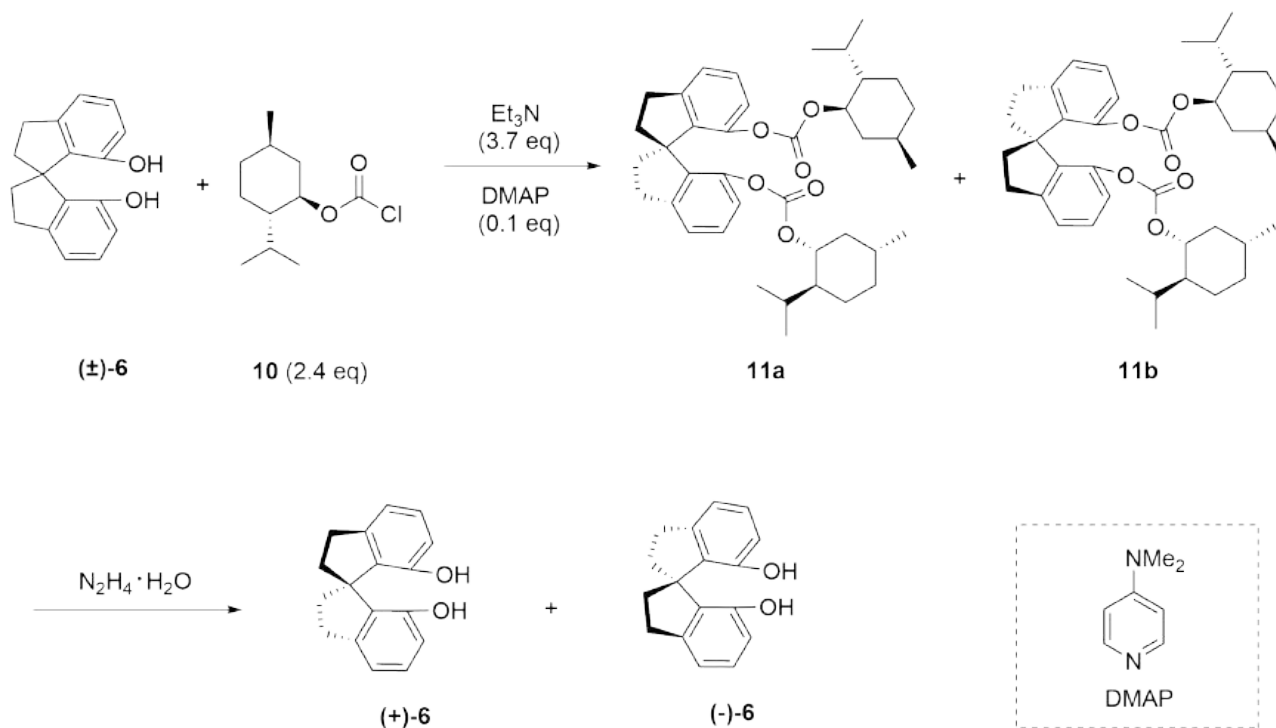| 8.1	**Draw** the structures of **1, 2, 4, 5**. (Stereochemistry is not considered)	16.0 pt

8.2	From the following reagents, **which** reagent **A** can **NOT** be used for the transformation of **8** to **9**? (a) NaBH(OAc)$_3$ (b) NaBH$_3$CN (c) NH$_2$NH$_2$, NaOH (d) NaBH$_4$	2.0 pt

The racemic spiro compound **6** reacts with (–)-menthyl chloroformate (**10**) to generate compounds **11a** and **11b**, which can be separated by column chromatography, followed by hydrazinolysis to obtain optically pure (+)-**6** and (–)-**6**.

Theory

Q8-3

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

Note:

eq = equivalent

8.3	**Choose** the correct statement below.

2.0 pt

(a) Compounds **11a** and **11b** are a pair of enantiomers.
(b) Compounds **11a** and **11b** are a pair of diastereomers.
(c) Compounds **11a** and **11b** are a pair of *cis-trans* isomers.
(d) Compounds **11a** and **11b** are a pair of conformational isomers.

Part B

The Ir-SpiroPAP was prepared by reaction of SpiroPAP with $[Ir(cod)Cl]_2$ (cod is cycloocta-1,5-diene) in MeOH under hydrogen as shown below.

Theory

Q8-4

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)
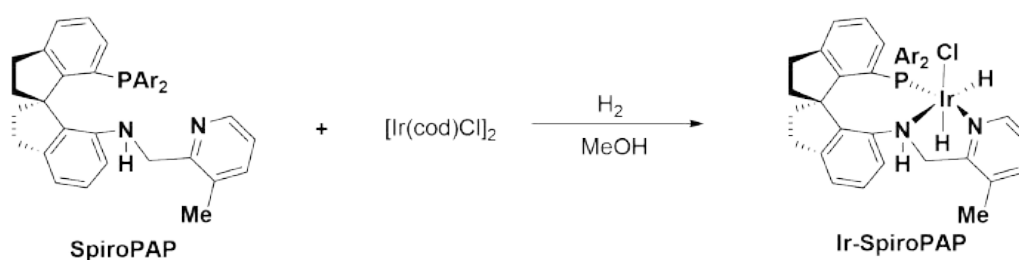
Note:

Ar = 3, 5-$(^t\text{Bu})_2\text{C}_6\text{H}_3$

8.4	**Write** the oxidation number of Ir in the catalyst Ir-SpiroPAP.	2.0 pt

8.5	**Write** the number of valence electrons of d orbitals for metal Ir in the catalyst Ir-SpiroPAP.	2.0 pt

The chiral spiro catalyst Ir-SpiroPAP was used for the asymmetric total synthesis of Mulinane-type diterpene **22** as shown below.
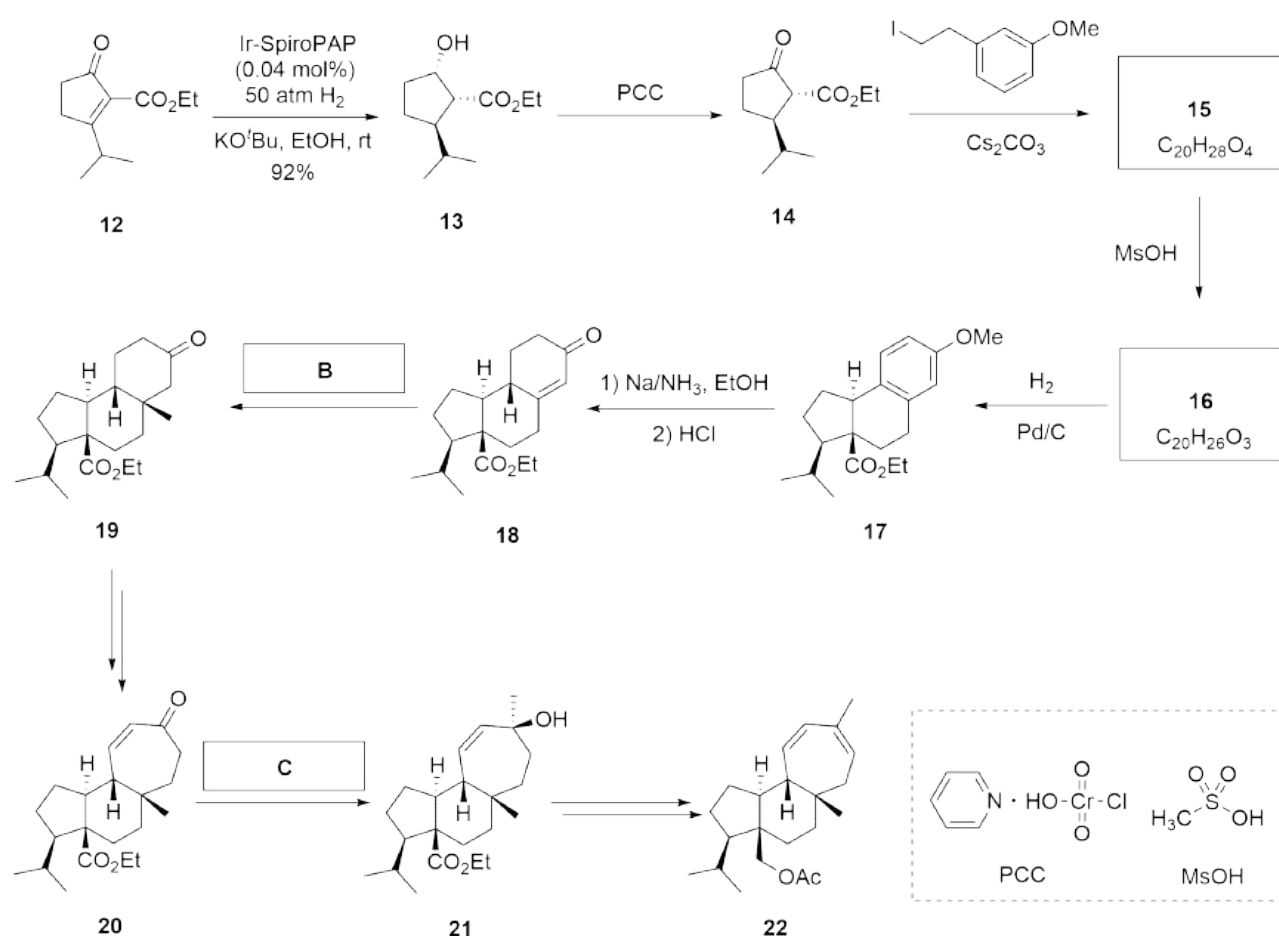
8.6	**Draw** the structures of **15** and **16**, including the appropriate stereochemistry.	8.0 pt

8.7	From the following reagents, <u>**choose**</u> the best for **B**. (a) MeLi/CeCl$_3$ (b) MeLi/CuI (c) MePh$_3$P$^+$I$^-$, ^{n}BuLi (d) Me$_3$S$^+$I$^-$, NaH	2.0 pt

8.8	From the following reagents, <u>**choose**</u> the best for **C**. (a) MeLi/CeCl$_3$ (b) MeLi/CuI (c) MePh$_3$P$^+$I$^-$, ^{n}BuLi (d) Me$_3$S$^+$I$^-$, NaH	2.0 pt

Amazing Chiral Spiro Catalyst

10% of the total								
Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	**Total**
Points	16	2	2	2	2	8	2	2	**36**
Score									

Part A

8.1 (16.0 pt)

1(4.0 pt)

2(4.0 pt)

4(4.0 pt)

5(4.0 pt)

8.2 (2.0 pt)
[   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)

8.3 (2.0 pt)

[ ] (a)   [ ] (b)   [ ] (c)   [ ] (d)

Part B

8.4 (2.0 pt)

_____

8.5 (2.0 pt)

_____

8.6 (8.0 pt)

15(4.0 pt)	**16**(4.0 pt)

8.7 (2.0 pt)

[ ] (a)   [ ] (b)   [ ] (c)   [ ] (d)

8.8 (2.0 pt)

[ ] (a)   [ ] (b)   [ ] (c)   [ ] (d)

Total Synthesis of Capitulactone

9% of the total					
Question	9.1	9.2	9.3	9.4	**Total**
Points	24	2	16	2	**44**
Score					

The plant of *Curculigo capitulata* grows in the Southern China and has long been used in traditional Chinese herbal medicine for the treatment of many diseases. Capitulactone (**1**) was isolated from the roots of *Curculigo capitulata*. Its structure with absolute configuration was unambiguously established by a combination of spectroscopic data and total synthesis.

Curculigo capitulata
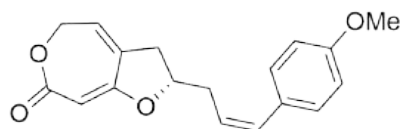
Capitulactone (**1**)

The total synthesis of **1** began with the iodination of commercially available 4-bromoveratrole **2** through a key intermediate **12** as shown in the following scheme.

Theory

Q9-2

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)
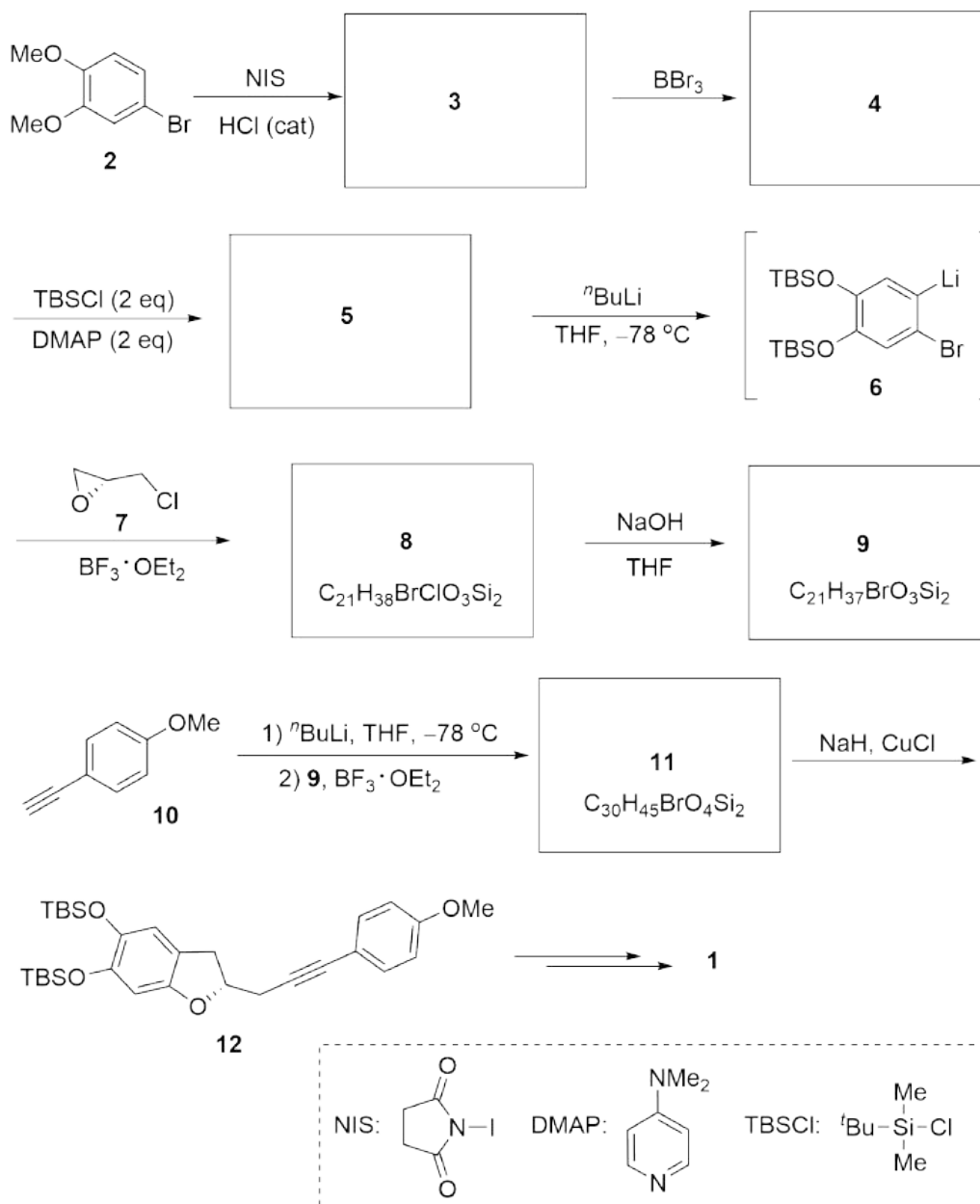
Note:

cat = catalyst

eq = equivalent

9.1	**Draw** the structures of compounds **3-5**, **8**, **9** and **11** and show the stereochemistry of any stereocenters.	24.0 pt

(*R*)-Epichlorohydrin (**7**) was prepared from (+)-mannitol (**13**) through a route as shown below.
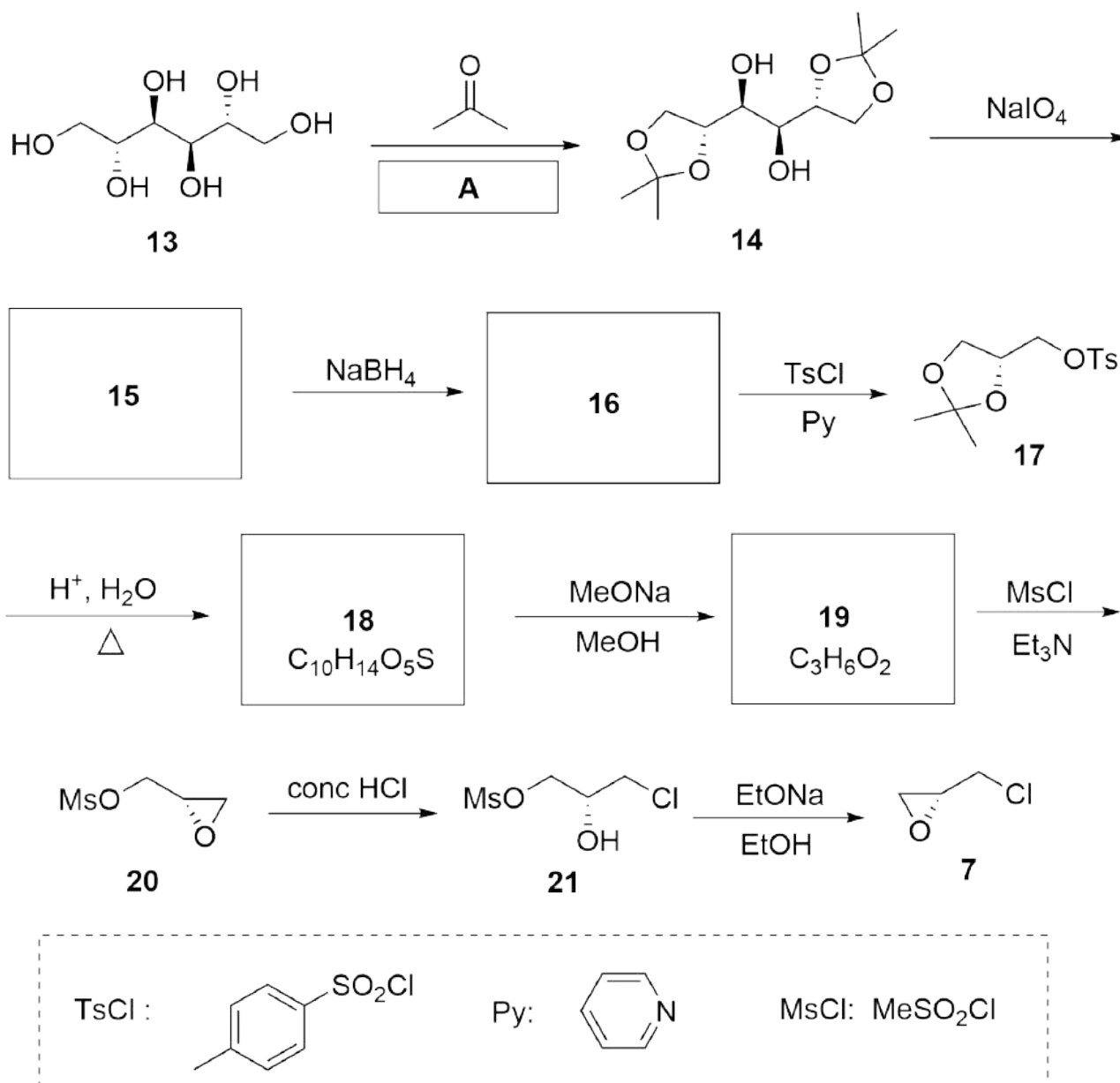
Note:

eq = equivalent

conc = concentrated

Theory

Q9-4

54ᵗʰ IChO2022
International Chemistry Olympiad
TIANJIN,CHINA

English (Official)

9.2	From the following conditions, **choose** the best for **A**. (a) Pyridine (b) 5% KOH/H$_2$O (c) 1% HCl/H$_2$O (d) Anhydrous ZnCl$_2$	2.0 pt

9.3	**Draw** the structures of intermediate products **15, 16, 18** and **19** and show the stereochemistry of any stereocenters.	16.0 pt

The diketal **14** can also be prepared by treating (+)-mannitol (**13**) with 2-methoxypropene (**23**) in the presence of catalytic amount of tolunesulfonic acid (TsOH) in anhydrous toluene. The model reaction is shown below.
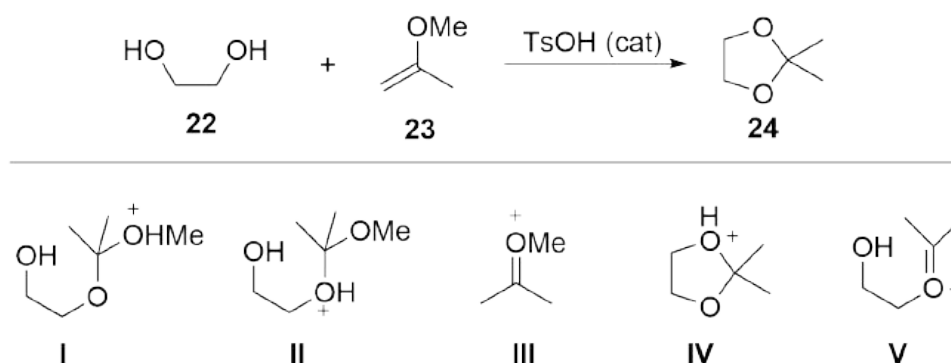
9.4	The proposed mechanism for this reaction involves key intermediates (**I-V**) as shown above, **choose** the correct order of the formation of the key intermediates during the reaction process. (a) **I, II, III, IV, V** (b) **III, II, I, V, IV** (c) **III, I, II, IV, V** (d) **III, I, II, V, IV**	2.0 pt

Total Synthesis of Capitulactone

9% of the total					
Question	9.1	9.2	9.3	9.4	**Total**
Points	24	2	16	2	**44**
Score					

9.1 (24.0 pt)

3 (4.0 pt)

4 (4.0 pt)

5 (4.0 pt)

8 (4.0 pt)

9.1 (cont.)

9 (4.0 pt)	**11** (4.0 pt)

9.2 (2.0 pt)

[   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)

9.3 (16.0 pt)

15 (4.0 pt)	**16** (4.0 pt)
18 (4.0 pt)	**19** (4.0 pt)

9.4 (2.0 pt)

[   ] (a)   [   ] (b)   [   ] (c)   [   ] (d)

[Marking Scheme] Rapid and Visual Nucleic Acid Testing for COVID-19

1.1 (1.0 pt)

> (d)

1.2 (1.0 pt)

> (a)

Theory-Marking Scheme

M1-2

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TIANJIN, CHINA

English (Official)

1.3 (4.0 pt)

The volume of a gold nanoparticle: $\quad$ 1 point

$$V_{NP} = \frac{4}{3}\pi \left(\frac{D}{2}\right)^3 = \frac{4}{3} \times 3.14 \times \left(\frac{30.0 \times 10^{-7}}{2}\right)^3 = 1.41 \times 10^{-17}\ \text{cm}^3\ \text{or}\ 1.41 \times 10^{-23}\ \text{m}^3$$

The mass of a gold nanoparticle: $\quad$ 1 point

$$m_{NP} = \rho V_{NP} = 19.3 \times 1.41 \times 10^{-17} = 2.72 \times 10^{-16}\ \text{g}$$

The number of gold atoms in each particle: $\quad$ 2 point

$$N = \frac{m_{NP}}{AW_{Au}} \cdot N_A = \frac{2.72 \times 10^{-16}}{197.0} \times 6.022 \times 10^{23} = 8.31 \times 10^5$$

OR $\quad$ 4 points

$$N = \frac{V_{NP}}{V_{\text{atom}}} = \frac{\pi \rho N_A D^3}{6M} = \frac{3.14 \times 19.3 \times 6.022 \times 10^{23} \times (30.0 \times 10^{-7})^3}{6 \times 197.0} = 8.34 \times 10^5$$

OR

The volume of a gold nanoparticle: $\quad$ 1 point

$$V_{NP} = \frac{4}{3}\pi \left(\frac{D}{2}\right)^3 = \frac{4}{3} \times 3.14 \times \left(\frac{30.0 \times 10^{-7}}{2}\right)^3 = 1.41 \times 10^{-17}\ \text{cm}^3\ \text{or}\ 1.41 \times 10^{-23}\ \text{m}^3$$

The mass of each gold atom: $\quad$ 1 point

$$m = \frac{AW_{Au}}{N_A} = \frac{197.0}{6.022 \times 10^{23}} = 3.271 \times 10^{-22}\ \text{g}$$

The volume of each gold atom: $\quad$ 1 point

$$V_{\text{atom}} = \frac{m}{\rho} = \frac{3.271 \times 10^{-22}}{19.3} = 1.69 \times 10^{-23}\ \text{cm}^3$$

The number of gold atoms in each particle: $\quad$ 1 point

$$N = \frac{V_{NP}}{V_{\text{atom}}} = \frac{1.41 \times 10^{-17}}{1.69 \times 10^{-23}} = 8.34 \times 10^5$$

4 points in total
−1 point for calculating error.

1.4 (4.0 pt)

The total number of gold atoms: 1 points

$$N_{\text{Total}} = \frac{5.2 \times 10^{-3}}{394} \times 6.022 \times 10^{23} = 7.9 \times 10^{18}$$

The concentration of gold nanoparticles: 2 points

$$C = \frac{N_{\text{Total}}}{NVN_A} = \frac{7.9 \times 10^{18}}{8.34 \times 10^5 \times 100 \times 10^{-3} \times 6.022 \times 10^{23}} = 1.6 \times 10^{-10}\,\text{mol}\,\text{L}^{-1}$$

The extinction coefficient: 1 points

$$\varepsilon = \frac{A}{lC} = \frac{0.800}{1 \times 1.6 \times 10^{-10}} = 5.0 \times 10^9\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$$

4 points in total
$-$1 point for each calculating error.

1.5 (4.0 pt)

$A_1 = \varepsilon l C_1 = \varepsilon l \dfrac{0.10 C_x}{1.0} = 0.400$ 1 point

$A_2 = \varepsilon l C_2 = \varepsilon l \dfrac{0.10 C_x + 2.0 \times 0.10}{1.0} = 0.900$ 1 point

OR $\dfrac{0.400}{0.900} = \dfrac{\dfrac{0.10 C_x}{1.0}}{\dfrac{0.10 C_x + 2.0 \times 0.10}{1.0}}$ 2 points

$C_x = 1.6\,\mu\text{g}\,\text{mL}^{-1}$ 2 points

4 points in total
$-$1 point for calculating error.

Theory-Marking Scheme

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

M2-1

English (Official)

[Marking Scheme] Chromium in Ancient and Modern Times

2.1 (2.0 pt)

A: 8 B: 16

2 points in total, each correct assignment 1 point

2.2 (1.0 pt)

Fe (or iron)

2.3 (6.0 pt)
Fe^{3+} : 7, Cr^{3+} : 9
Solution 1:
Assume there are x Fe ions (including Fe^{2+} and Fe^{3+}) and y Cr^{3+} ions in a cubic cell, then
$$\frac{x}{y} = \frac{63.6 \times (52.00 \times 2 + 16.00 \times 3)}{36.4 \times (55.85 \times 2 + 16.00 \times 3)}$$
which gives the result: $\frac{x}{y} = 1.66$
Considering that the total amount of the cations in each crystal cell is 24, it can be obtained
$$(1 + 1.66)y = 24$$
which gives the result: $y \approx 9$
Thus, the amount of Fe^{3+} occupying the octahedral vacancies is
$$16 - 9 = 7$$

Solution 2:
Assume there are x Fe ions (including Fe^{2+} and Fe^{3+}) in the final compound, then, the number of Cr^{3+} should be $3-x$ because the summary of A+B should be 3 in AB_2O_4, and the formula of the compound should be $Fe_xCr_{3-x}O_4$, then
$$\frac{x}{3-x} = \frac{63.6 \times (52.00 \times 2 + 16.00 \times 3)}{36.4 \times (55.85 \times 2 + 16.00 \times 3)} = \frac{5}{3}$$
which gives the result: $x = 1.875$
Accordingly, Fe^{2+} in the tetrahedral vacancies is 1, and the number of Fe^{3+} in the octahedral vacancies is
$$x - 1 = 1.875 - 1 = 0.875$$
and the number of Cr^{3+} occupying the octahedral is
$$3 - x = 3 - 1.875 = 1.125$$
In one unit cell, there are 8 Fe^{2+}, thus the numbers of Fe^{3+} and Cr^{3+} are
$$\frac{8}{1} \times 0.875 = 7 \qquad \text{and} \qquad \frac{8}{1} \times 1.125 = 9$$
respectively.

6 points in total
2 points for the correct molar ratio of Fe/Cr
1 point for the correct result of the amount of Cr^{3+}
1 point for the correct result of the total amount of Fe
1 point for the correct result of the amount of Fe^{3+}
1 point for the correct result of the number of Fe^{3+} and Cr^{3+} in the **B** sites of one unit cell

2.4 (1.0 pt)

Na_2CrO_4

2.5 (2.0 pt)

$Na_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + H_2O + 2NaHSO_4$
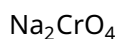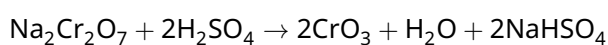
Ionic form is acceptable.
−1 point if the stoichiometry is incorrect.

2.6 (1.0 pt)

(A)

2.7 (1.0 pt)

(B)

2.8 (5.0 pt)
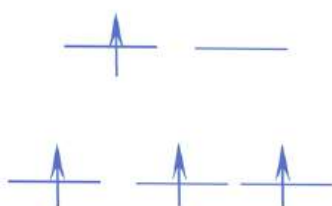
$CFSE = 0 - E_{octa} = 0 - [(-2/5\Delta_o) \times 3 + 3/5\Delta_o] = 3/5\Delta_o = 9600 \text{ cm}^{-1}$

5 points in total

1 point for the correct energy level of the five $3d$ orbitals in octahedral crystal field.

1 point for the correct electron configuration on the energy level lines.

1 point for the correct equation of CFSE.

1 point for the result of CFSE with Δ_o.

1 point for the result of CFSE with cm^{-1}.

2.9 (2.0 pt)

$\mu = \sqrt{4(4+2)}\,\mu_B = 4.9\,\mu_B$

2 points

[Marking Scheme] Capture and Transformation of Carbon Dioxide

---

3.1 (2.0 pt)
A: $CaCO_3$ **B**: CaO
2 points in total; 1 point for each

3.2 (5.0 pt)

step 1: (2a) $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

or $2OH^- + CO_2 \longrightarrow CO_3^{2-} + H_2O$

(2b) $NaOH + CO_2 \longrightarrow NaHCO_3$

or $OH^- + CO_2 \longrightarrow HCO_3^-$

or $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

or $CO_3^{2-} + CO_2 + H_2O \longrightarrow 2HCO_3^-$

step 2: (2c) $Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$

(2d) $NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + NaOH + H_2O$

step 3: (2e) $CaCO_3 \longrightarrow CaO + CO_2$

5 points in total; 1 point for each equation (2a) $\sim$ (2e)

3.3 (2.0 pt)

A: $H_2 \rightarrow 2H^+ + 2e^-$

C: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

2 points in total; 1 point for each equation

3.4 (3.0 pt)

1 $H^+ + CO_3^{2-} \longrightarrow HCO_3^-$

2 $H^+ + HCO_3^- \longrightarrow H_2CO_3$

3 $H_2CO_3 \longrightarrow H_2O + CO_2$

3 points in total; 1 point for each equation.

Theory-Marking Scheme

54ᵗʰ IChO2022
International Chemistry Olympied
TIANJIN,CHINA

M3-2
English (Official)

3.5 (2.0 pt)
[✓] (a)　　　　[ ] (b)　　　　[ ] (c)　　　　[✓] (d)　　　　[ ] (e)
2 points in total; 1 point for each correct selection.

If wrong item(s) is/are included, −1 point for each till the total point is zero, no negative score.

3.6 (8.0 pt)

Rate of H^+ production:

$r(H^+) = 60 \; s\,min^{-1} \times 2.00\,A/(96485\,C\,mol^{-1})$　　　　　　　　**2 points**

$= 1.24 \times 10^{-3}\,mol\,min^{-1} = 1.24\,mmol\,min^{-1}$　　　　　　　　**1 point**

Input rate of HCO_3^- to zone B:

$r(HCO_3^-) = 0.10\,mol\,L^{-1} \times 10.0\,mL\,min^{-1} = 1.0\,mmol\,min^{-1}$

Input rate of CO_3^{2-} to zone B:

$r(CO_3^{2-}) = 0.050\,mol\,L^{-1} \times 10.0\,mL\,min^{-1} = 0.50\,mmol\,min^{-1}$　　　**1 point**

$H^+ + CO_3^{2-} \longrightarrow HCO_3^-$　　　　　$H^+ + HCO_3^- \longrightarrow CO_2 + H_2O$

The amount of dissolved CO_2 in the flow:

$10.0\,mL\,min^{-1} \times 0.033\,mol\,L^{-1} = 0.33\,mmol\,min^{-1}$　　　　　**1 point**

Rate of CO_2 production:

$r(CO_2) = r(H^+) - r(CO_3^{2-}) - 0.33\,mmol\,min^{-1}$　　　　　　**2 points**

$= 1.24\,mmol\,min^{-1} - 0.50\,mmol\,min^{-1} - 0.33\,mmol\,min^{-1} = 0.41\,mmol\,min^{-1}$　　**1 point**
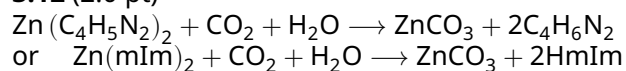
8 points in total
Some of the steps in the derivation and in the calculation may be taken implicitly or simultaneously.
As long as they are correct, full marks will be scored for each of the partial steps.

3.7 (2.0 pt)
$Zn_{24}(C_4H_5N_2)_{36}^{12+}$ or $Zn_{24}(C_4H_5N_2)_{60}^{12-}$
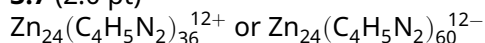
2 points in total

Expression $Zn_{24}(mIm)_{36}^{12+}$ or $Zn_{24}(mIm)_{60}^{12-}$ is acceptable.

3.8 (2.0 pt)
$Zn_{12}(C_4H_5N_2)_{24}$
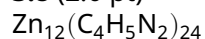
2 points in total

Expression $Zn_{12}(mIm)_{24}$ or $Zn_{12}C_{96}H_{120}N_{48}$ is acceptable.

3.9 (5.0 pt)

$$M_{Zn(C_4H_5N_2)_2} = [65.38 + (12.01 \times 4 + 1.01 \times 5 + 14.02 \times 2) \times 2]\,\text{g mol}^{-1} = 227.6\,\text{g mol}^{-1} \qquad \text{1 point}$$

$$S = \frac{2 \times 4\pi r^2 \times N_A \times 1\,\text{g}}{12 \times M_{Zn(C_4H_5N_2)_2}}$$

$$= \frac{2 \times 4 \times 3.14 \times \left(\dfrac{1.16 \times 10^{-9}\,\text{m}}{2}\right)^2 \times 6.02 \times 10^{23}\,\text{mol}^{-1} \times 1\,\text{g}}{12 \times [65.38 + (12.01 \times 4 + 1.01 \times 5 + 14.01 \times 2) \times 2]\,\text{g mol}^{-1}}$$

$$= \frac{50.8 \times 10^5}{12 \times 227.6}\,\text{m}^2 = 1.86 \times 10^3\,\text{m}^2$$

4 points: 2 point for the correct formula (1 point for the coefficient 2), 1 for properly introducing data, 1 for correct calculation result.

5 points in total.

Some of the steps in the derivation and in the calculation may be taken implicitly or simultaneously. As long as they are correct, full marks will be scored for each of the partial steps.

3.10 (7.0 pt)

Volume of one spherical cage:

$$V_{\text{Cage}} = (4/3) \times 3.14 \times (1.16\,\text{nm}/2)^3 = 0.817\,\text{nm}^3 \qquad \text{1 point}$$

Volume of the unit cell:

$$V_{\text{cell}} = (1.632\,\text{nm})^3 = 4.347\,\text{nm}^3 \qquad \text{1 point}$$

Porosity:

$$R = 2 \times V_{\text{Cage}}/V_{\text{cell}} = 2 \times 0.817\,\text{nm}^3/4.347\,\text{nm}^3 = 0.376 \qquad \text{2 points}$$

1 point for the coefficient 2

$$V_{\text{p}} = \frac{2 \times V_{\text{cage}} \times N_{\text{A}} \times 1\,\text{g}}{12 \times M_{\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2}} = \frac{\frac{4}{3}\pi r^3 \times N_{\text{A}} \times 1\,\text{g}}{6 \times M_{\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2}}$$

$$= \frac{0.817 \times 10^{-21}\,\text{cm}^3 \times 6.02 \times 10^{23}\,\text{mol}^{-1} \times 1\,\text{g}}{6 \times 227.6\,\text{g mol}^{-1}} = 0.360\,\text{cm}^3 \qquad \text{3 points}$$

3 points: 1 for the correct formula, 1 for properly introducing data; 1 for correct calculation result

7 points in total.

Some of the steps in the derivation and in the calculation may be taken implicitly or simultaneously. As long as they are correct, full marks will be scored for each of the partial steps.

3.11 (2.0 pt)
I   (b)   **II**   (d)
2 points in total, 1 point for each correct selection.

3.12 (2.0 pt)
$\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{ZnCO}_3 + 2\text{C}_4\text{H}_6\text{N}_2$
or $\text{Zn}(\text{mIm})_2 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{ZnCO}_3 + 2\text{HmIm}$
2 points in total

Theory-Marking Scheme

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

M4-1

English (Official)

[Marking Scheme] A New Journey for Ancient Sulfur

4.1 (2.0 pt)

$$3\,FeS_2 + 2\,O_2 \xrightarrow{\Delta} 6\,S + Fe_3O_4 \quad \text{or} \quad 12\,FeS_2 + 8\,O_2 \xrightarrow{\Delta} 3\,S_8 + 4\,Fe_3O_4$$
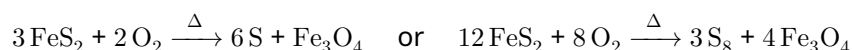
No penalty will be given if the heating symbol on the reaction arrow is missing.
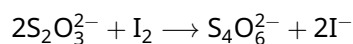−1 point if the stoichiometry is incorrect.

4.2 (4.0 pt)

(a) $Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$ (2 points)

or

$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2I^-$

(b) $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$ (2 points)

or

$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$
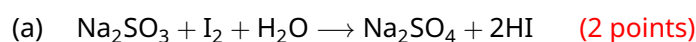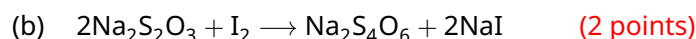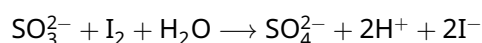
No partial point will be given if NaOH is present for (a).
No partial point will be given if the oxidation product is not $Na_2S_4O_6$ or $S_4O_6^{2-}$ for (b).
−1 point if the stoichiometry is incorrect for each equation.

4.3 (4.0 pt)

$0.05122\,mol\,L^{-1} \times 50.00\,mL = 2.561\,mmol$ (1 point)

$\frac{1}{2} \times 0.1012\,mol\,L^{-1} \times 18.47\,mL = 0.9346\,mmol$ (1 point)

$(2.561\,mmol - 0.9346\,mmol) \times 10^{-3} \times 20 \times 32.06\,g\,mol^{-1} = 1.043\,g$ (1 point)

$\frac{1.043\,g}{(1.043\,g + 17.6\,g)} \times 100\% = 5.59\%$ (1 point)

4 points in total
For each calculation, consider whether the logic for solving this question is correctly established;
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.
If the calculation is based on the incorrect equation answered in 4.2 (b), no penalty will be given when the calculation is correct.

Theory-Marking Scheme

M4-2

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

4.4 (3.0 pt)

(a) $S_8 + 16Li^+ + 16e^- \longrightarrow 8Li_2S$ **(2 points)**

(b) $Li \longrightarrow Li^+ + e^-$ or $16Li \longrightarrow 16Li^+ + 16e^-$ **(1 point)**
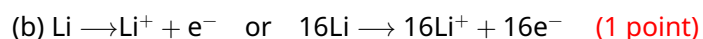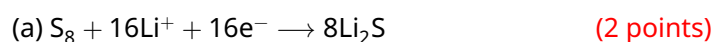
3 points in total
No partial point will be given if the cathode and anode reactions are reversed.
-1 point if the stoichiometry is incorrect for (a).
No penalty will be given if the equation is written as $S + 2e^- \longrightarrow S^{2-}$ for (a).
No penalty will be given if the equation is written as $S + 2Li^+ + 2e^- \longrightarrow Li_2S$ for (a).
No penalty will be given if e^- is written as e.

4.5 (1.0 pt)

$$\frac{8 \times 32.06}{16 \times 6.941} = 2.3$$

1 point in total
0.5 point will be given if the ratio is presented in reverse order.
No penalty will be given if the ratio is in reverse order but the cathode and the anode are correctly identified.

Theory-Marking Scheme

M4-3

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

4.6 (5.0 pt)

The total energy of the LIB is $3.8\,\text{V} \times 3.110\,\text{A h} \times 3600\,\text{s/h} = 4.25 \times 10^4\,\text{J}$ **(1 point)**

Energy consumed by the mobile phone per hour is $\dfrac{4.25 \times 10^4\,\text{J}}{22\,\text{h}} = 1.93 \times 10^3\,\text{J h}^{-1}$ **(1 point)**

The capacity of the ideal lithium-sulfur battery pack is

$\dfrac{23\,\text{g} \times 16 \times 96485\,\text{C mol}^{-1}}{8 \times 32.06\,\text{g mol}^{-1}} = \dfrac{23\,\text{g} \times 2 \times 96485\,\text{C mol}^{-1}}{32.06\,\text{g mol}^{-1}} = 1.4 \times 10^5\,\text{C}$ **(1 point)**

The total energy of the ideal lithium-sulfur battery pack is

$4.2\,\text{V} \times 1.4 \times 10^5\,\text{C} = 5.9 \times 10^5\,\text{J}$ **(1 point)**

After a full charge, the new battery pack can provide energy for the phone to play videos

continuously for: $\dfrac{5.9 \times 10^5\,\text{J}}{1.93 \times 10^3\,\text{J h}^{-1}} = 306\,\text{h}$ **(1 point)**

5 points in total
For each calculation, consider whether the logic for solving this question is correctly established;
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.
−1 point if any other unit than asked unit is used in the answer.
No penalty will be given if the result is 301 h without rounded calculations.

4.7 (2.0 pt)

$(2n - 2)\,\text{Li} + \text{Li}_2\text{S}_n \longrightarrow n\text{Li}_2\text{S}$
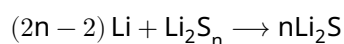
−1 point if the stoichiometry is incorrect.
No penalty will be given if n is written as 3-8 and the stoichiometry is correct.

4.8 (4.0 pt)

$Li_2S_6(I)(DME) \longrightarrow Li_2S_6(II)(DME)$
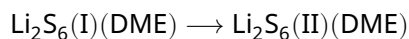
$\Delta G^{\ominus}_{I \rightarrow II} = \Delta G^{\ominus}_{d1}(I) - \Delta G^{\ominus}_{d1}(II) = 20.68 \text{ kJ mol}^{-1} - 18.92 \text{ kJ mol}^{-1} = 1.76 \text{ kJ mol}^{-1}$

or

$\Delta G^{\ominus}_{I \rightarrow II} = \Delta G^{\ominus}_{dr}(I) - \Delta G^{\ominus}_{dr}(II) = 45.13 \text{ kJ mol}^{-1} - 43.37 \text{ kJ mol}^{-1} = 1.76 \text{ kJ mol}^{-1}$ (1 point)

$\Delta G^{\ominus}_{I \rightarrow II} = -RT \ln K^{\ominus}_{I \rightarrow II}$ (1 point)

$K^{\ominus}_{I \rightarrow II} = \exp \left(-\dfrac{1.76 \text{ kJ mol}^{-1} \times 1000}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} \right) = 0.492$ (1 point)

$K^{\ominus}_{I \rightarrow II} = \dfrac{[Li_2S_6(II)]/c^{\ominus}}{[Li_2S_6(I)]/c^{\ominus}} = \dfrac{[Li_2S_6(II)]}{[Li_2S_6(I)]} = 0.492$ (1 point)
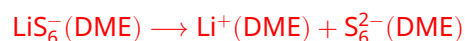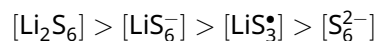
4 points in total
For each calculation, consider whether the logic for solving this question is correctly established;
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.

4.9 (5.0 pt)

$\dfrac{[\text{Li}_2\text{S}_6(\text{II})]}{[\text{Li}_2\text{S}_6(\text{I})]} = 0.492$, $[\text{Li}_2\text{S}_6(\text{II})] = 0.492[\text{Li}_2\text{S}_6(\text{I})]$
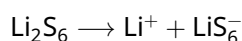
$\text{Li}_2\text{S}_6 \longrightarrow \text{Li}^+ + \text{LiS}_6^-$

$K_{\text{d1}}^{\ominus} = \dfrac{[\text{Li}^+][\text{LiS}_6^-]}{[\text{Li}_2\text{S}_6]} = \dfrac{[\text{Li}^+][\text{LiS}_6^-]}{[\text{Li}_2\text{S}_6(\text{I})] + [\text{Li}_2\text{S}_6(\text{II})]}$ **(1 point)**

$K_{\text{d1}}^{\ominus} = \dfrac{[\text{Li}^+][\text{LiS}_6^-]}{1.492[\text{Li}_2\text{S}_6(\text{I})]} = \dfrac{K_{\text{d1}}^{\ominus}(\text{I})}{1.492}$ **(1 point)**

or

$K_{\text{d1}}^{\ominus} = \dfrac{[\text{Li}^+][\text{LiS}_6^-]}{3.03[\text{Li}_2\text{S}_6(\text{II})]} = \dfrac{K_{\text{d1}}^{\ominus}(\text{II})}{3.03}$

or

$K_{\text{d1}}^{\ominus} = \dfrac{[\text{Li}^+][\text{LiS}_6^-]}{[\text{Li}_2\text{S}_6(\text{I})] + [\text{Li}_2\text{S}_6(\text{II})]} = \dfrac{1}{\dfrac{1}{K_{\text{d1}}^{\ominus}(\text{I})} + \dfrac{1}{K_{\text{d1}}^{\ominus}(\text{II})}}$

$\text{Li}_2\text{S}_6(\text{I}) \longrightarrow \text{Li}^+ + \text{LiS}_6^-$, $\Delta G_{\text{d1}}^{\ominus}(\text{I}) = -RT \ln K_{\text{d1}}^{\ominus}(\text{I})$ **(1 point)**

$K_{\text{d1}}^{\ominus}(\text{I}) = \exp\left(-\dfrac{20.68\,\text{kJ mol}^{-1} \times 1000}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}}\right) = 2.37 \times 10^{-4}$ **(1 point)**

or

$\text{Li}_2\text{S}_6(\text{II}) \longrightarrow \text{Li}^+ + \text{LiS}_6^-$, $\Delta G_{\text{d1}}^{\ominus}(\text{II}) = -RT \ln K_{\text{d1}}^{\ominus}(\text{II})$

$K_{\text{d1}}^{\ominus}(\text{II}) = \exp\left(-\dfrac{18.92\,\text{kJ mol}^{-1} \times 1000}{8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}}\right) = 4.84 \times 10^{-4}$

$K_{\text{d1}}^{\ominus} = \dfrac{2.37 \times 10^{-4}}{1.492} = 1.59 \times 10^{-4}$ **(1 point)**

or

$K_{\text{d1}}^{\ominus} = \dfrac{4.84 \times 10^{-4}}{3.03} = 1.59 \times 10^{-4}$

or

$K_{\text{d1}}^{\ominus} = \dfrac{1}{\dfrac{1}{K_{\text{d1}}^{\ominus}(\text{I})} + \dfrac{1}{K_{\text{d1}}^{\ominus}(\text{II})}} = \dfrac{1}{\dfrac{1}{2.37 \times 10^{-4}} + \dfrac{1}{4.84 \times 10^{-4}}} = 1.59 \times 10^{-4}$

5 points in total
For each calculation, consider whether the logic for solving this question is correctly established;
If not, no points will be given.
-1 point if the answer is not correct due to miscalculation.

Theory-Marking Scheme

M4-6

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

4.10 (4.0 pt)

$$[Li_2S_6] > [LiS_6^-] > [LiS_3^\bullet] > [S_6^{2-}]$$

$$LiS_6^-(DME) \longrightarrow Li^+(DME) + S_6^{2-}(DME)$$

$$\Delta G_{d2}^\ominus = -RT \ln K_{d2}^\ominus, \quad K_{d2}^\ominus = \exp\left(-\frac{100.55 \, \text{kJ mol}^{-1} \times 1000}{8.314 \, \text{J mol}^{-1} \, \text{K}^{-1} \times 298.15 \, \text{K}}\right) = 2.418 \times 10^{-18}$$

$$Li_2S_6 \rightarrow 2LiS_3^\bullet$$
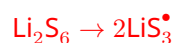
$$K_{dr}^\ominus = \frac{\left[LiS_3^\bullet\right]^2}{[Li_2S_6]} = \frac{\left[LiS_3^\bullet\right]^2}{[Li_2S_6(I)] + Li_2S_6(II)} = \frac{\left[LiS_3^\bullet\right]^2}{1.492 \, [Li_2S_6(I)]} = \frac{K_{dr}^\ominus(I)}{1.492}$$

$$Li_2S_6(I) \rightarrow 2LiS_3^\bullet, \Delta G_{dr}^\ominus(I) = -RT \ln K_{dr}^\ominus(I)$$

$$K_{dr}^\ominus(I) = \exp\left(-\frac{45.13 \, \text{kJ mol}^{-1} \times 1000}{8.314 \, \text{J mol}^{-1} \, \text{K}^{-1} \times 298.15 \, \text{K}}\right) = 1.24 \times 10^{-8}$$

$$K_{dr}^\ominus = \frac{1.24 \times 10^{-8}}{1.492} = 8.31 \times 10^{-9}$$

4 points in total
+1 point if $[Li_2S_6]$ is in the first blank, but (2),(3),(4) and $[LiS_6^-]$, $[LiS_3^\bullet]$, $[S_6^{2-}]$ are not in one-to-one correspondence.
(2), (3), (4) and $[LiS_6^-]$, $[LiS_3^\bullet]$, $[S_6^{2-}]$ must be in one-to-one correspondence, e.g. -2 points if $[LiS_3^\bullet] > [LiS_6^-] > [S_6^{2-}]$.

Theory-Marking Scheme

M4-7

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

4.11 (6.0 pt)
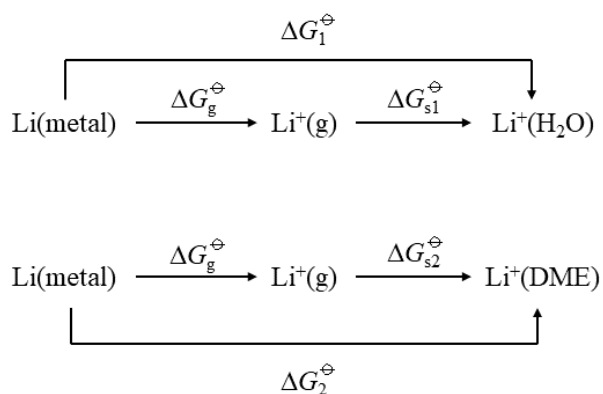
$\Delta G_1^{\ominus} = \Delta G_g^{\ominus} + \Delta G_{s1}^{\ominus}$ (1)   **(1 point)**

$\Delta G_2^{\ominus} = \Delta G_g^{\ominus} + \Delta G_{s2}^{\ominus}$ (2)   **(1 point)**

$(2) - (1)$: $\Delta G_2^{\ominus} - \Delta G_1^{\ominus} = \Delta G_{s2}^{\ominus} - \Delta G_{s1}^{\ominus}$ **(1 point)**

$\text{Li(metal)} \longrightarrow \text{Li}^+(\text{H}_2\text{O}) + \text{e}^-$, $\Delta G_1^{\ominus} = nFE^{\ominus}(\text{Li}^+(\text{H}_2\text{O})/\text{Li})$ **(1 point)**

$\text{Li(metal)} \longrightarrow \text{Li}^+(\text{DME}) + \text{e}^-$, $\Delta G_2^{\ominus} = nFE^{\ominus}(\text{Li}^+(\text{DME})/\text{Li})$ **(1 point)**

$nFE^{\ominus}(\text{Li}^+(\text{DME})/\text{Li}) = nFE^{\ominus}(\text{Li}^+(\text{H}_2\text{O})/\text{Li}) - \Delta G_{s1}^{\ominus} + \Delta G_{s2}^{\ominus}$

$E^{\ominus}(\text{Li}^+(\text{DME})/\text{Li}) = -3.040 - \dfrac{[(-116.9\,\text{kJ mol}^{-1}) - (-114.6\,\text{kJ mol}^{-1})] \times 1000}{96485\,\text{C mol}^{-1}} = -3.016\,\text{V}$ **(1 point)**

6 points in total
For each calculation, consider whether the logic for solving this question is correctly established.
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.

Theory-Marking Scheme

M4-8

54ᵗʰ IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

4.12 (5.0 pt)

Assume $\left[S_4^{2-}\right] = c_1$, the original concentration of Li_2S is c_0
According to the charge balance:

$$2c_0 = 1 \times \left[S_3^{\bullet-}\right] + 2 \times \left[S_4^{2-}\right] + 2 \times \left[S_5^{2-}\right] + 2 \times \left[S_6^{2-}\right] + 2 \times \left[S_7^{2-}\right] + 2 \times \left[S_8^{2-}\right]$$ (1 point)

$$2c_0 = 17.50c_1 + 1.00 \times 2c_1 + 4.50 \times 2c_1 + 55.00 \times 2c_1 + 5.00 \times 2c_1 + 0.75 \times 2c_1 = 150c_1$$

$$c_0 = 75c_1$$ (1point)

According to the material balance:

$$c_0 + \frac{4.81\ \text{mg}}{32.07\ \text{g}\,\text{mol}^{-1} \times 10.00\ \text{mL}}$$

$$= 17.50 \times 3c_1 + 1.00 \times 4c_1 + 4.50 \times 5c_1 + 55.00 \times 6c_1 + 5.00 \times 7c_1 + 0.75 \times 8c_1$$ (1 point)

$$75c_1 + 0.0150\ \text{mmol}\,\text{mL}^{-1} = 450c_1$$ (1 point)

$$c_1 = 4.00 \times 10^{-5}\ \text{mmol}\,\text{mL}^{-1}$$

$$m(Li_2S) = 75 \times 4.00 \times 10^{-5}\ \text{mmol}\,\text{mL}^{-1} \times 10.00\ \text{mL} \times 45.96\ \text{g}\,\text{mol}^{-1} = 1.38\ \text{mg}$$ (1 point)

5 points in total
For each calculation, consider whether the logic for solving this question is correctly established.
If not, no points will be given.
−1 point if the answer is not correct due to miscalculation.

[Marking Scheme] Interconversion among Nitrogen Oxides

15% of the total										
Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	5.10	**Total**
Points	4	4	2	4	3	8	4	6	4	6	**45**
Score											

5.1 (4.0 pt)

Using the definition of $K_{c1} = \dfrac{[N_2O_2]}{[NO]^2}$, $[N_2O_2] = K_{c1}[NO]^2$ is obtained.

Thus, $r_+ = k_2[N_2O_2][O_2] = k_2 K_{c1}[NO]^2[O_2]$

4 points in total
1 point for the correct expression of K_{c1}
1 point for the expression of r_+ with $[N_2O_2]$ and $[O_2]$
1 point for the correct $[N_2O_2]$
1 point for the correct r_+

5.2 (4.0 pt)

Combining $K_{c1} = \exp(M - N/T)$, $k_2 = A_2 \exp\left(-\dfrac{E_{a,2}}{RT}\right)$ and $k_+ = k_2 K_{c1}$,

$k_+ = k_2 K_{c1} = A_2 \exp\left(-\dfrac{E_{a,2}}{RT}\right) \exp\left(M - \dfrac{NR}{RT}\right) = A_2 \exp(M) \exp\left(-\dfrac{E_{a,2} + NR}{RT}\right)$.

Comparing this equation with Arrhenius equation,

$A_+ = A_2 \exp(M)$ and $E_{a+} = E_{a,2} + NR$ are obtained.

4 points in total
1 point for the correct expression of k_2
1 point for the correct expression of k_+ with $E_{a,2}$, A_2, M and N
1 point for the correct expression of A_+
1 point for the correct expression of E_{a+}

5.3 (2.0 pt)

Calculation:

According to Arrhenius equation, $\ln \dfrac{k_+(T_2)}{k_+(T_1)} = \dfrac{E_{a+}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ is obtained.

Thus, $k_+(700\ \text{K}) = 6.86 \times 10^5\ \text{L}^2\ \text{mol}^{-2}\ \text{min}^{-1}$

2 points in total
If $k_+(700\ \text{K})$ is incorrect due to miscalculation, 1 point will be deducted.

Theory-Marking Scheme

M5-2

54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

English (Official)

5.4 (4.0 pt)
Calculation:
Because $\Delta_r H_m^\ominus$ and $\Delta_r S_m^\ominus$ do not change with temperature,
$\Delta_r H_m^\ominus(600K)$
$= \Delta_r H_m^\ominus(298K)$
$= 2\Delta_f H_m^\ominus(NO_2, 298K) - \Delta_f H_m^\ominus(NO, 298K) - \Delta_r H_m^\ominus(O_2, 298K)$
$= -116.4\,kJ\,mol^{-1}$

$\Delta_r S_m^\ominus(600K)$
$= \Delta_r S_m^\ominus(298K)$
$= 2S_m^\ominus(NO_2, 298K) - 2S_m^\ominus(NO, 298K) - S_m^\ominus(O_2, 298K)$

$-146.6\,J\,K^{-1}\,mol^{-1}$
For a thermostatic process, $\Delta G = \Delta H - T\Delta S$, thus $\Delta_r G_m^\ominus(600\ K) = -28.44\ kJ\ mol^{-1}$
Using the equation of $K_p^\ominus = \exp(-\Delta_r G_m^\ominus/RT)$, $K_p^\ominus(600\ K) = 299.2$ is obtained.

4 points in total
1 point for the correct value of $\Delta_r H_m^\ominus$ (600 K)
1 point for the correct value of $\Delta_r S_m^\ominus$ (600 K)
1 point for the correct value of $\Delta_r G_m^\ominus$ (600 K) or the correct relationship among $\Delta_r H_m^\ominus$ (600 K),
$\Delta_r S_m^\ominus$ (600 K) and $K_p^\ominus$ (600 K)
1 point for the correct value of $K_p^\ominus$ (600 K)
If any miscalculation exists, 1 point will be deducted.

5.5 (3.0 pt)
Calculation:
Using the equation of $\Delta_r U_m^\ominus = \Delta_r H_m^\ominus - \sum \nu RT$ and $\sum \nu$ value of -1 ($\nu_{NO_2} - \nu_{NO} - \nu_{O_2} = 2-2-1 = -1$),
$\Delta_r U_m^\ominus(600\ K) = -111.4\ kJ\ mol^{-1}$ is obtained.

3 points in total
1 point for the correct relationship between $\Delta_r U_m^\ominus$ and $\Delta_r H_m^\ominus$
1 point for the correct value of $\Sigma\nu$
1 point for the correct value of $\Delta_r U_m^\ominus$ (600 K)
If $\Delta_r U_m^\ominus$ (600 K) is incorrect due to miscalculation, 0.5 points will be deducted

Theory-Marking Scheme

M5-3

English (Official)

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International Chemistry Olympiad
TIANJIN,CHINA

5.6 (6.0 pt)

Calculation:

When chemical equilibrium is reached, $K_c = \dfrac{[NO_2]_{eq}^2}{[NO]_{eq}^2\,[O_2]_{eq}}$ and $r_{-eq} = r_{+eq}$.

Thus, $r_{-eq} = r_{+eq} = k_+[NO]_{eq}^2\,[O_2]_{eq} = k_+\dfrac{[NO_2]_{eq}^2}{K_c} = k_-\,[NO_2]_{eq}^2$

Therefore, $r_- = k_-\,[NO_2]^2$

Using the equation of $K_c = K_p^\ominus \left(\dfrac{RT}{p^\ominus}\right)^{-\sum_B \nu_B}$ and $K_p^\ominus$ (600 K) value of 299.2, $K_c = 1.49 \times 10^4$ L mol^{-1} is obtained.

According to $k_- = k_+/K_c$, the value of $k\_$ is calculated to be 44.4 L mol^{-1} min^{-1} If the $K_p^\ominus$ (600 K) value is used as 350.0, the result should be 38.0.

8 points in total
1 point for the consideration of $r_{-eq} = r_{+eq}$
2 points for the correct expression of r_-
1 point for the correct relationship among k_+, K and k_-
4 points for the correct value of k_-
If $K_p^\ominus$ instead of K_c is used, 2 points will be deducted
If $k\_$ is incorrect due to miscalculation, 1 point will be deducted

---

5.7 (4.0 pt)

Calculation:

According to the stoichiometry of the reaction and setting $p_{NO_2} = 0.8p_0, p_{NO} = 0.2p_0$ and $p_{O_2} = 0.1p_0$ are obtained.

$$K_p^\ominus = \frac{\left(p_{NO_2}/p^\ominus\right)^2}{\left(p_{NO}/p^\ominus\right)^2\left(p_{O_2}/p^\ominus\right)} = \frac{(0.8p_0/p^\ominus)^2}{(0.2p_0/p^\ominus)^2\,(0.1p_0/p^\ominus)} = \frac{160p^\ominus}{p_0}$$

Therefore, $p_0 = 53.5$ kPa. $p_{total} = p_{NO_2} + p_{NO} + p_{O_2} = 1.1p_0 = 58.8$ kPa

If the $K_p^\ominus$ (600 K) value is used as 350.0, the result of 50.3 kPa is obtained.

4 points in total
1 point for the expression of $K_p^\ominus$. If $p^\ominus$ is omitted, no penalty.
1 point for the correct ratio among p_{NO_2}, p_{NO} and p_{O_2}
2 points for the correct value of p_{total}
If p_{total} is incorrect due to miscalculation, 1 point will be deducted

Theory-Marking Scheme

M5-4

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5.8 (6.0 pt)
The given mechanism involves a pre-equilibrium:
$$r_{S+1} = r_{S-1}, k_{S+1}[O_2]\theta_v^2 = k_{S-1}\theta_O^2, \theta_O/\theta_v = (k_{S+1}[O_2]/k_{S-1})^{0.5}$$
$$r_{S+2} = r_{S-2}, k_{S+2}[NO]\theta_v = k_{S-2}\theta_{NO}, \theta_{NO}/\theta_v = k_{S+2}[NO]/k_{S-2}$$
$$r_{S+4} = r_{S-4}, k_{S+4}\theta_{NO_2} = k_{S-4}[NO_2]\theta_v, \theta_{NO_2}/\theta_v = k_{S-4}[NO_2]/k_{S+4}$$
Because $\theta_v + \theta_{NO} + \theta_{NO_2} + \theta_O = 1$, using the ratios among these coverages,
$$\theta_v = \frac{1}{1 + (k_{S+1}[O_2]/k_{S-1})^{0.5} + k_{S+2}[NO]/k_{S-2} + k_{S-4}[NO_2]/k_{S+4}} \text{ is obtained.}$$

6 points in total
1 point for the correct expression of θ_0/θ_v
1 point for the correct expression of θ_{NO}/θ_v
1 point for the correct expression of θ_{NO2}/θ_v
1 point for the utilization of the normalized condition
2 points for the correct expression of θ_v
If no derivation is provided, 6 points for the correct expression of θ_v
One of the numerator and the four parts of the denominator of this expression is wrong, 4 points;
two of them are wrong, 2 points; three or more are wrong, 0 point.

5.9 (4.0 pt)

(B)

4 points for choosing (B)
2 points for choosing (A)
0 points for other choices

5.10 (6.0 pt)

(B)

6 points for choosing (B)
0 points for other choices

Theory-Marking Scheme

54th IChO2022
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M6-1

English (Official)

[Marking Scheme] Enabling Phosphines

6.1 (3.0 pt)

R

3 points in total;
3 points for assigning as *R*

6.2 (6.0 pt)
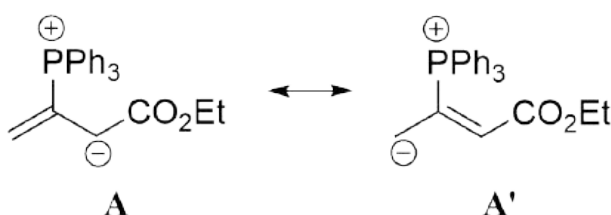
6 points in total.
3 points for each;
no points if any structure containing C=P is given:
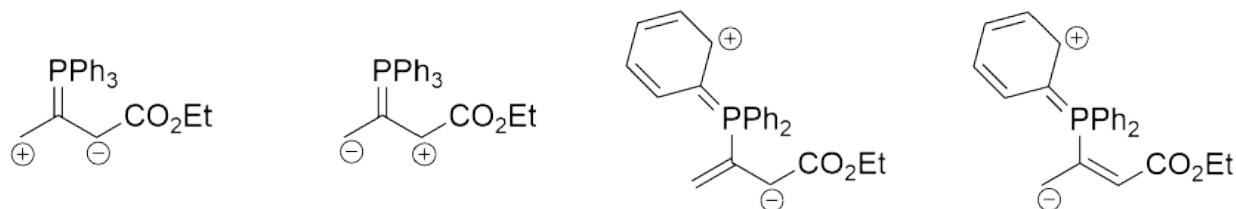
6.3 (8.0 pt)
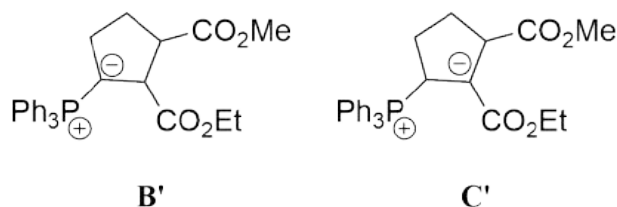
8 points in total.
4 points for each.
Reasonable resonance structures of **B'** and **C'** are also acceptable.
1 point is given if structures with two methyl esters or two ethyl esters.

6.4 (5.0 pt)
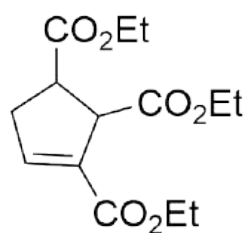
6

5 points in total.
2 points if the isomerized structure is given:
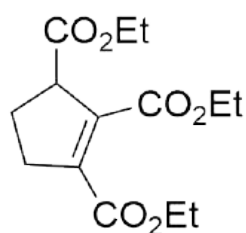
6.5 (6.0 pt)
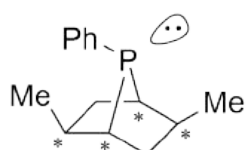
P2

6 points in total.
6 points for 4 correct asterisks, 1.5 points for each;
—1.5 points for every wrong asterisk till 0 points.

6.6 (3.0 pt)
90:10
3 points in total;
3 points for the correct answer: 90/10 or 9/1 or 9

6.7 (5.0 pt)
(d)
5 points in total;
5 points for choosing (d)

Organic Molecules in Life

7.1 (12.0 pt)

7   **9**   **12**
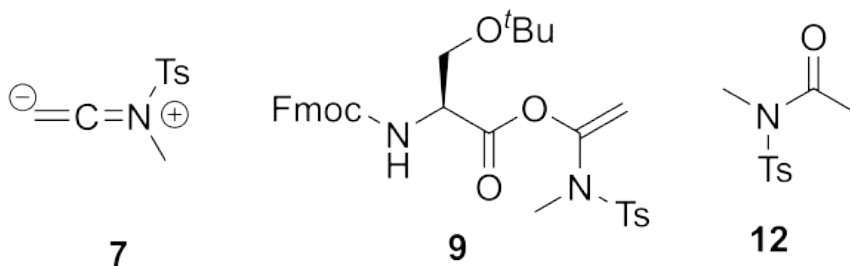
12 points in total.
4 points for each;
2 points for the enantiomer of **9**, or the structure missing the chirality is given;
2 points if the enol form of **12** is given:
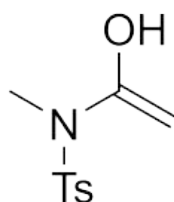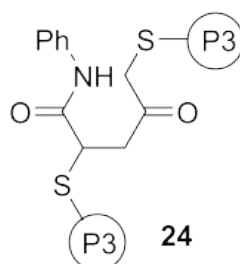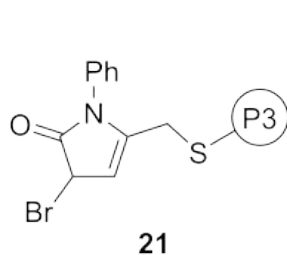
Theory-Marking Scheme

M7-2

54th IChO2022
International Chemistry Olympiad
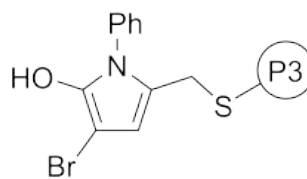TIANJIN, CHINA

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7.2 (8.0 pt)
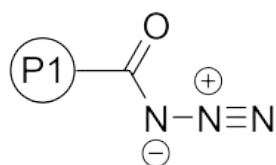
15   **16**
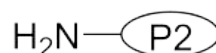
8 points in total.
4 points for each;
4 points for the resonance structures of **15** or if azide is written as N_3:
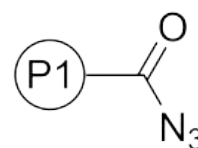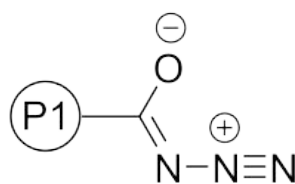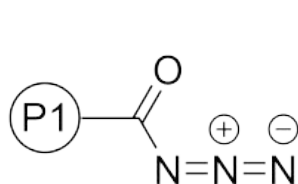
2 points for its protonated form:
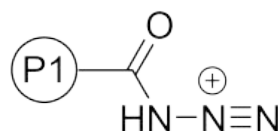
1 point if the nitrosonation on the nitrogen linked to carbonyl is given:
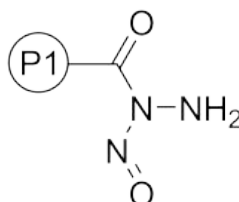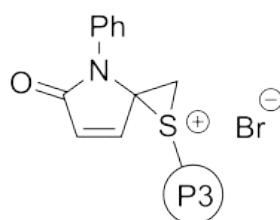
7.3 (12.0 pt)
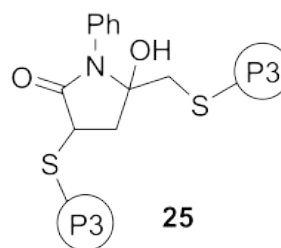
12 points in total.
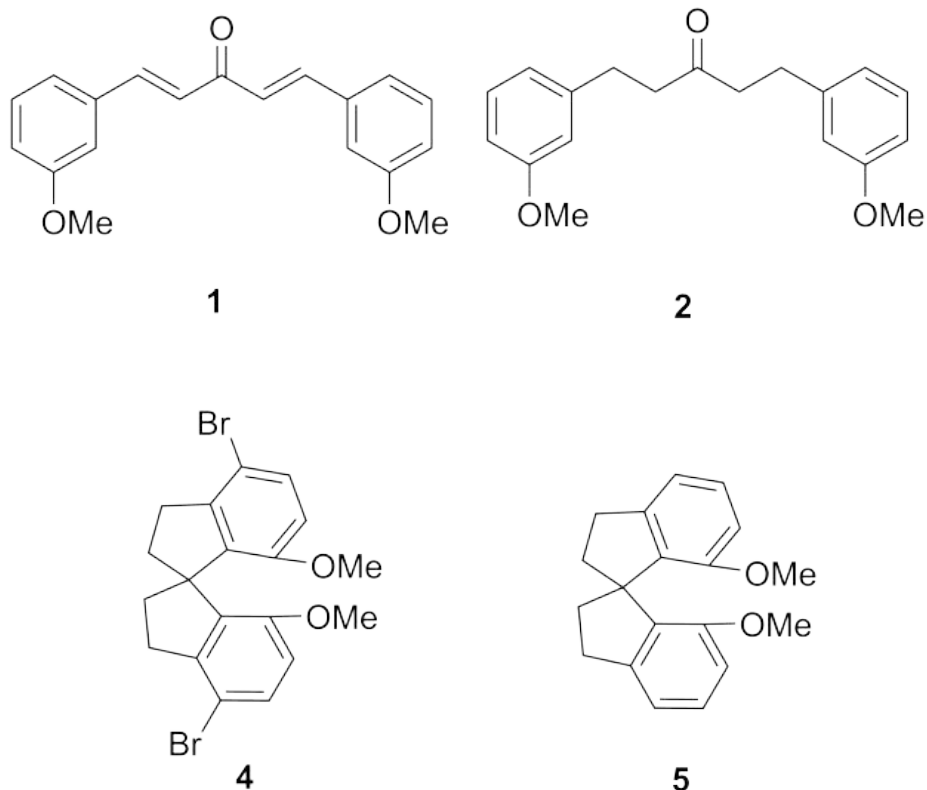4 points for the isomers of **21**:
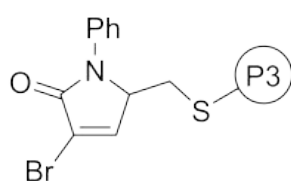
2 points if the form of NGP is given:

1 point if the second protein is added at the β position of amide group, and no double punishment for **24** and **25**.

[Marking Scheme] Amazing Chiral Spiro Catalyst

8.1 (16.0 pt)

16 points in total.
4 points for each correct structure as shown above.
4 points if the *cis* isomer of **1** is given
2 points if the regioisomer of **4** is given

8.2 (2.0 pt)
(c)
2 points in total;
2 points for choosing (c)

8.3 (2.0 pt)
(b)
2 points in total;
2 points for choosing (b)

Theory-Marking Scheme

M8-2

54th IChO2022
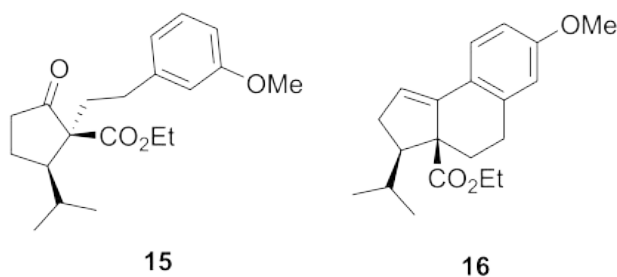International Chemistry Olympiad
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8.4 (2.0 pt)
Ir(III) or +3
2 points in total;
2 points for Ir(III) or +3

8.5 (2.0 pt)
6
2 points in total;
2 points for 6

8.6 (8.0 pt)

15   16

8 points in total.
4 points for each;
2 points for correct skeleton, missing or wrong stereochemistry;
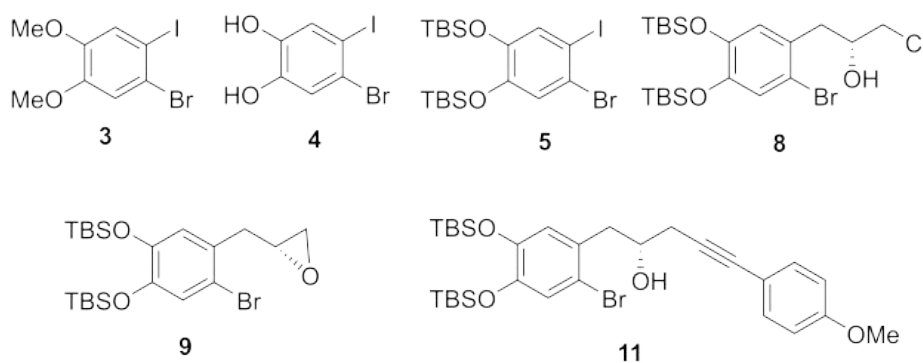2 points if the regioisomer of **16** is given

8.7 (2.0 pt)
(b)
2 points in total;
2 points for choosing (b)

8.8 (2.0 pt)
(a)
2 points in total;
2 points for choosing (a)

Theory-Marking Scheme

M9-1

54th IchO2022
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English (Official)

[Marking Scheme] Total Synthesis of Capitulactone

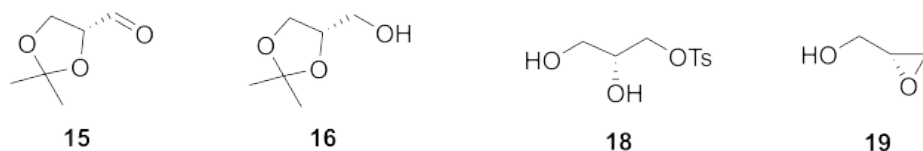| 9% of the total					
Question	9.1	9.2	9.3	9.4	**Total**
Points	24	2	16	2	**44**
Score					

9.1 (24.0 pt)

24 points in total.
4 points for each;
2 points for each structure of **8**, **9** or **11** with missing or wrong stereochemistry.

9.2 (2.0 pt)
(d)
2 points in total;
2 points for choosing (d)

9.3 (16.0 pt)

16 points in total.
4 points for each;
2 points if structure with missing or wrong stereochemistry is given.

9.4 (2.0 pt)
(b)
2 points in total;
2 points for choosing (b)