

54th IChO2022

QUESTIONS and MARKING SCHEMES



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



54th IChO2022

International Chemistry Olympiad



TIANJIN, CHINA

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!

Theory



G0-3

English (Official)

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:	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant:	$R = 8.31446 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard pressure:	$p^\ominus = 1 \text{ bar} = 10^5 \text{ Pa}$
Standard atmospheric pressure:	$p_{\text{atm}} = 1 \text{ atm} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa}$
Zero of the Celsius scale:	273.15 K
Faraday constant:	$F = 9.6485 \times 10^4 \text{ C mol}^{-1}$
Planck's constant:	$h = 6.626 \times 10^{-34} \text{ J s}$
Mass of electron:	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Speed of light:	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
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:	$\Delta S = Q_{\text{rev}}/T$
Gibbs free energy:	$G = H - TS$ $\Delta G^\ominus = -RT \ln K^\ominus$ $\Delta G^\ominus = -nFE_{\text{cell}}^\ominus$ $\Delta G = \Delta G^\ominus + RT \ln Q$
Reaction quotient:	$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$
<i>For a reaction $a[\text{A}] + b[\text{B}] \rightleftharpoons c[\text{C}] + d[\text{D}]$</i>	
Nernst equation:	$E = E^\ominus - \frac{RT}{nF} \ln \frac{c_{\text{red}}}{c_{\text{ox}}}$
Langmuir isotherm equation:	$\theta = aP/(1 + aP)$
Arrhenius equation:	$k = Ae^{-E_a/RT}$
Integrated rate law:	
Zero order:	$[\text{A}] = [\text{A}]_0 - kt$
First order:	$\ln[\text{A}] = \ln[\text{A}]_0 - kt$
Second order:	$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$

Theory



G0-5

English (Official)

Half-life time for a first order process:

$$t_{1/2} = \frac{\ln 2}{k_1}$$

Half-life time for a second order process ($A + A \rightarrow B$):

$$t_{1/2} = \frac{1}{k[A]_0}$$

Lambert-Beer equation:

$$A = \epsilon l C$$

Electric work:

$$W = U I t = U Q$$

Quantity of electric charge:

$$Q = I t$$

Volume of a sphere:

$$V = \frac{4}{3} \pi r^3$$

Surface area of a sphere:

$$S = 4 \pi r^2$$

Theory



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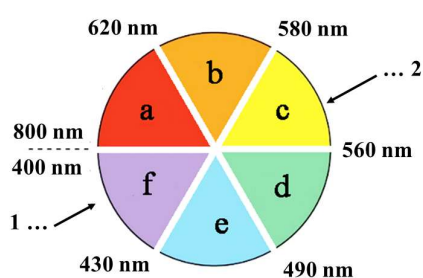
G0-6

English (Official)

Periodic Table

1	2	13	14	15	16	17	18
1 H 1.008	2 He 4.003	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3 Li 6.941	4 Be 9.012	11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06
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
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
55 Cs 132.9	56 Ba 137.3	57-71 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2
87 Fr -	88 Ra -	89-103 Ac -	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -
111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -
129 Nh -	130 Ds -	131 Rg -	132 Cn -	133 Nh -	134 Fl -	135 Mc -	136 Lv -
153 Nh -	154 Ds -	155 Rg -	156 Cn -	157 Nh -	158 Fl -	159 Mc -	160 Lv -
173 Nh -	174 Ds -	175 Rg -	176 Cn -	177 Nh -	178 Fl -	179 Mc -	180 Lv -
193 Nh -	194 Ds -	195 Rg -	196 Cn -	197 Nh -	198 Fl -	199 Mc -	200 Lv -
213 Nh -	214 Ds -	215 Rg -	216 Cn -	217 Nh -	218 Fl -	219 Mc -	220 Lv -
233 Nh -	234 Ds -	235 Rg -	236 Cn -	237 Nh -	238 Fl -	239 Mc -	240 Lv -
253 Nh -	254 Ds -	255 Rg -	256 Cn -	257 Nh -	258 Fl -	259 Mc -	260 Lv -
273 Nh -	274 Ds -	275 Rg -	276 Cn -	277 Nh -	278 Fl -	279 Mc -	280 Lv -
293 Nh -	294 Ds -	295 Rg -	296 Cn -	297 Nh -	298 Fl -	299 Mc -	300 Lv -
313 Nh -	314 Ds -	315 Rg -	316 Cn -	317 Nh -	318 Fl -	319 Mc -	320 Lv -
333 Nh -	334 Ds -	335 Rg -	336 Cn -	337 Nh -	338 Fl -	339 Mc -	340 Lv -
353 Nh -	354 Ds -	355 Rg -	356 Cn -	357 Nh -	358 Fl -	359 Mc -	360 Lv -
373 Nh -	374 Ds -	375 Rg -	376 Cn -	377 Nh -	378 Fl -	379 Mc -	380 Lv -
393 Nh -	394 Ds -	395 Rg -	396 Cn -	397 Nh -	398 Fl -	399 Mc -	400 Lv -
413 Nh -	414 Ds -	415 Rg -	416 Cn -	417 Nh -	418 Fl -	419 Mc -	420 Lv -
433 Nh -	434 Ds -	435 Rg -	436 Cn -	437 Nh -	438 Fl -	439 Mc -	440 Lv -
453 Nh -	454 Ds -	455 Rg -	456 Cn -	457 Nh -	458 Fl -	459 Mc -	460 Lv -
473 Nh -	474 Ds -	475 Rg -	476 Cn -	477 Nh -	478 Fl -	479 Mc -	480 Lv -
493 Nh -	494 Ds -	495 Rg -	496 Cn -	497 Nh -	498 Fl -	499 Mc -	500 Lv -
513 Nh -	514 Ds -	515 Rg -	516 Cn -	517 Nh -	518 Fl -	519 Mc -	520 Lv -
533 Nh -	534 Ds -	535 Rg -	536 Cn -	537 Nh -	538 Fl -	539 Mc -	540 Lv -
553 Nh -	554 Ds -	555 Rg -	556 Cn -	557 Nh -	558 Fl -	559 Mc -	560 Lv -
573 Nh -	574 Ds -	575 Rg -	576 Cn -	577 Nh -	578 Fl -	579 Mc -	580 Lv -
593 Nh -	594 Ds -	595 Rg -	596 Cn -	597 Nh -	598 Fl -	599 Mc -	600 Lv -
613 Nh -	614 Ds -	615 Rg -	616 Cn -	617 Nh -	618 Fl -	619 Mc -	620 Lv -
633 Nh -	634 Ds -	635 Rg -	636 Cn -	637 Nh -	638 Fl -	639 Mc -	640 Lv -
653 Nh -	654 Ds -	655 Rg -	656 Cn -	657 Nh -	658 Fl -	659 Mc -	660 Lv -
673 Nh -	674 Ds -	675 Rg -	676 Cn -	677 Nh -	678 Fl -	679 Mc -	680 Lv -
693 Nh -	694 Ds -	695 Rg -	696 Cn -	697 Nh -	698 Fl -	699 Mc -	700 Lv -
713 Nh -	714 Ds -	715 Rg -	716 Cn -	717 Nh -	718 Fl -	719 Mc -	720 Lv -
733 Nh -	734 Ds -	735 Rg -	736 Cn -	737 Nh -	738 Fl -	739 Mc -	740 Lv -
753 Nh -	754 Ds -	755 Rg -	756 Cn -	757 Nh -	758 Fl -	759 Mc -	760 Lv -
773 Nh -	774 Ds -	775 Rg -	776 Cn -	777 Nh -	778 Fl -	779 Mc -	780 Lv -
793 Nh -	794 Ds -	795 Rg -	796 Cn -	797 Nh -	798 Fl -	799 Mc -	800 Lv -
813 Nh -	814 Ds -	815 Rg -	816 Cn -	817 Nh -	818 Fl -	819 Mc -	820 Lv -
833 Nh -	834 Ds -	835 Rg -	836 Cn -	837 Nh -	838 Fl -	839 Mc -	840 Lv -
853 Nh -	854 Ds -	855 Rg -	856 Cn -	857 Nh -	858 Fl -	859 Mc -	860 Lv -
873 Nh -	874 Ds -	875 Rg -	876 Cn -	877 Nh -	878 Fl -	879 Mc -	880 Lv -
893 Nh -	894 Ds -	895 Rg -	896 Cn -	897 Nh -	898 Fl -	899 Mc -	900 Lv -
913 Nh -	914 Ds -	915 Rg -	916 Cn -	917 Nh -	918 Fl -	919 Mc -	920 Lv -
933 Nh -	934 Ds -	935 Rg -	936 Cn -	937 Nh -	938 Fl -	939 Mc -	940 Lv -
953 Nh -	954 Ds -	955 Rg -	956 Cn -	957 Nh -	958 Fl -	959 Mc -	960 Lv -
973 Nh -	974 Ds -	975 Rg -	976 Cn -	977 Nh -	978 Fl -	979 Mc -	980 Lv -
993 Nh -	994 Ds -	995 Rg -	996 Cn -	997 Nh -	998 Fl -	999 Mc -	1000 Lv -

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.

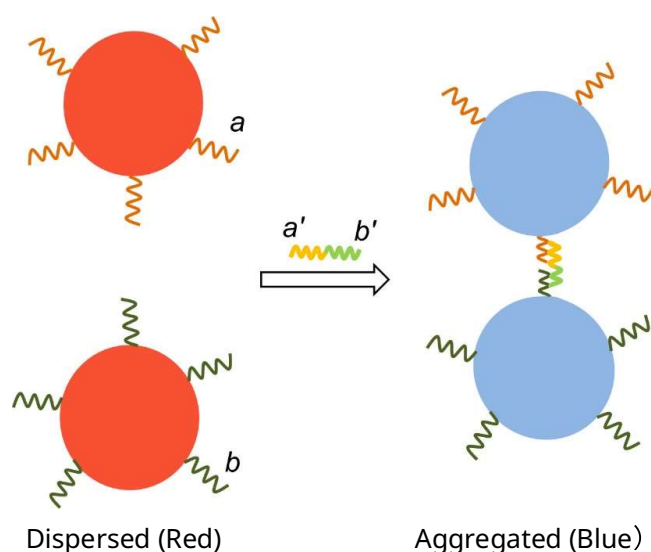
Figure 0.1

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.



- 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



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Q1-2

English (Official)

- 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 $\rho = 19.3 \text{ g cm}^{-3}$).

- 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) ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $M_W = 394$) and reducing substances (such as sodium citrate). 5.2 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ 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 $2.0 \mu\text{g mL}^{-1}$ 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

Theory



A1-1

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						

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)

$\epsilon =$ _____ $\text{L mol}^{-1} \text{cm}^{-1}$

1.5 (4.0 pt)

$C_X =$ _____ $\mu\text{g mL}^{-1}$

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.

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.

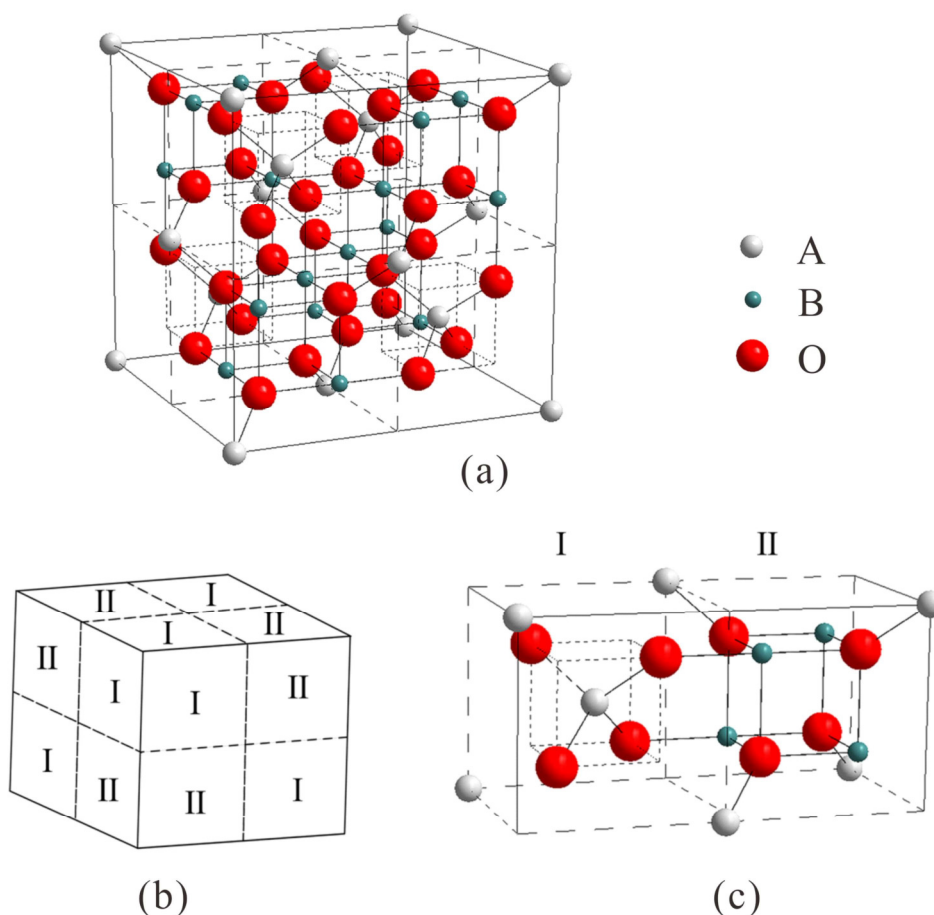


Figure 2.1 Illustration of spinel structure

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.

Theory



Q2-3

English (Official)

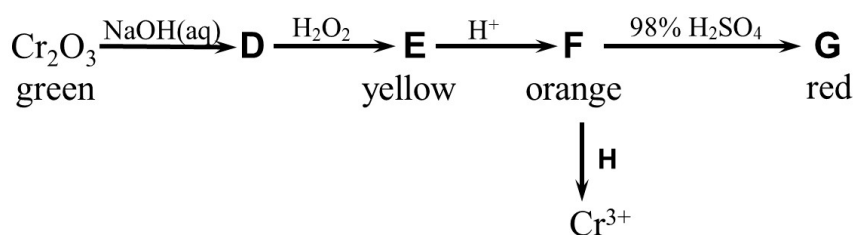
2.2 In **reaction (I)**, which element is reduced?

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.



2.4 Write the chemical formula of **E**.

1.0 pt

2.5 Write the reaction equation of **F** $\rightarrow$ **G**.

2.0 pt

2.6 Choose the agent which could be **H**.

1.0 pt

- (A) FeSO_4
- (B) FeCl_3
- (C) ZnSO_4
- (D) CuSO_4

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) species is the core in the pre-catalyst (**1**), which is proposed to be reduced quickly into a six-coordinated Cr(II) species (**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 |

Theory



A2-1

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										

2.1 (2.0 pt)

A : _____ B : _____

2.2 (1.0 pt)

2.3 (6.0 pt)

Theory



A2-2

English (Official)

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)

2.8 (5.0 pt)

CFSE = _____ cm^{-1}

2.9 (2.0 pt)

μ = _____ μ_{B}

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													

Climate change is one of the most critical global challenges nowadays. The increase of CO₂ concentration in the atmosphere has been recognized as the primary driver of global warming. The study of the capture and transformation of CO₂ has attracted considerable attention.

Direct air capture (DAC) technology which aims to extract CO₂ directly from ambient air is promising. The conventional method of DAC is wet scrubbing with alkaline hydroxide solutions (typically NaOH), where CO₂ 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 CO₂ and another white compound **B** (**step 3**). Finally, calcium hydroxide can be generated by the hydration of **B**. This process is highly energy-demanding. ($\text{H}_2\text{CO}_3 : K_{a1} = 4.5 \times 10^{-7}, K_{a2} = 4.7 \times 10^{-11}$)

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 CO₂ gas could be recovered that is suitable for storage or utilization. The process is based on a H₂-recycling electrochemical system (HRES), as shown in **Figure 3.1**.

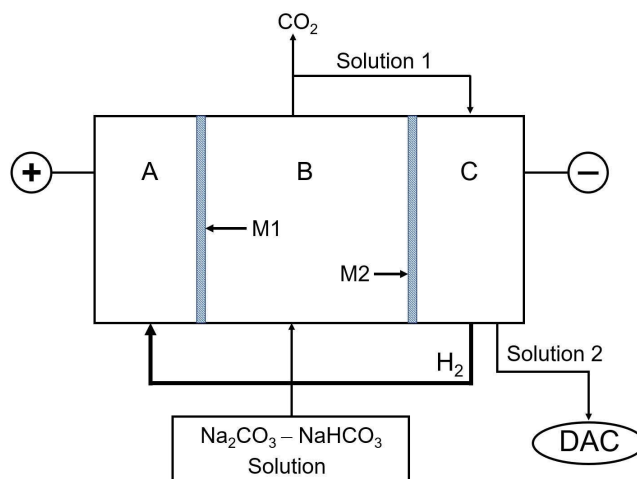


Figure 3.1 Schematic drawing of the experimental setup

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. 2.0 pt

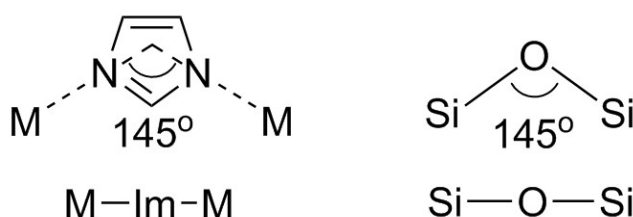
- (a) H^+ ions permeate through M1 from A to B.
- (b) H^+ ions permeate through M2 from B to C.
- (c) Na^+ ions permeate through M1 from B to A.
- (d) Na^+ ions permeate through M2 from B to C.
- (e) Both H^+ and Na^+ ions can permeate through M1 and M2.

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 ($0.050 \text{ mol L}^{-1} Na_2CO_3$ - $0.10 \text{ mol L}^{-1} NaHCO_3$) 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

materials for the capture and utilization of CO₂. The structures of ZIFs resemble zeolites. They form 3D frameworks with tetrahedrally coordinated metal ions (e.g. Zn²⁺, Co²⁺) 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 Zn²⁺ with 2-methylimidazole (CH₃(C₃N₂H₃), HmIm). It crystallizes 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.

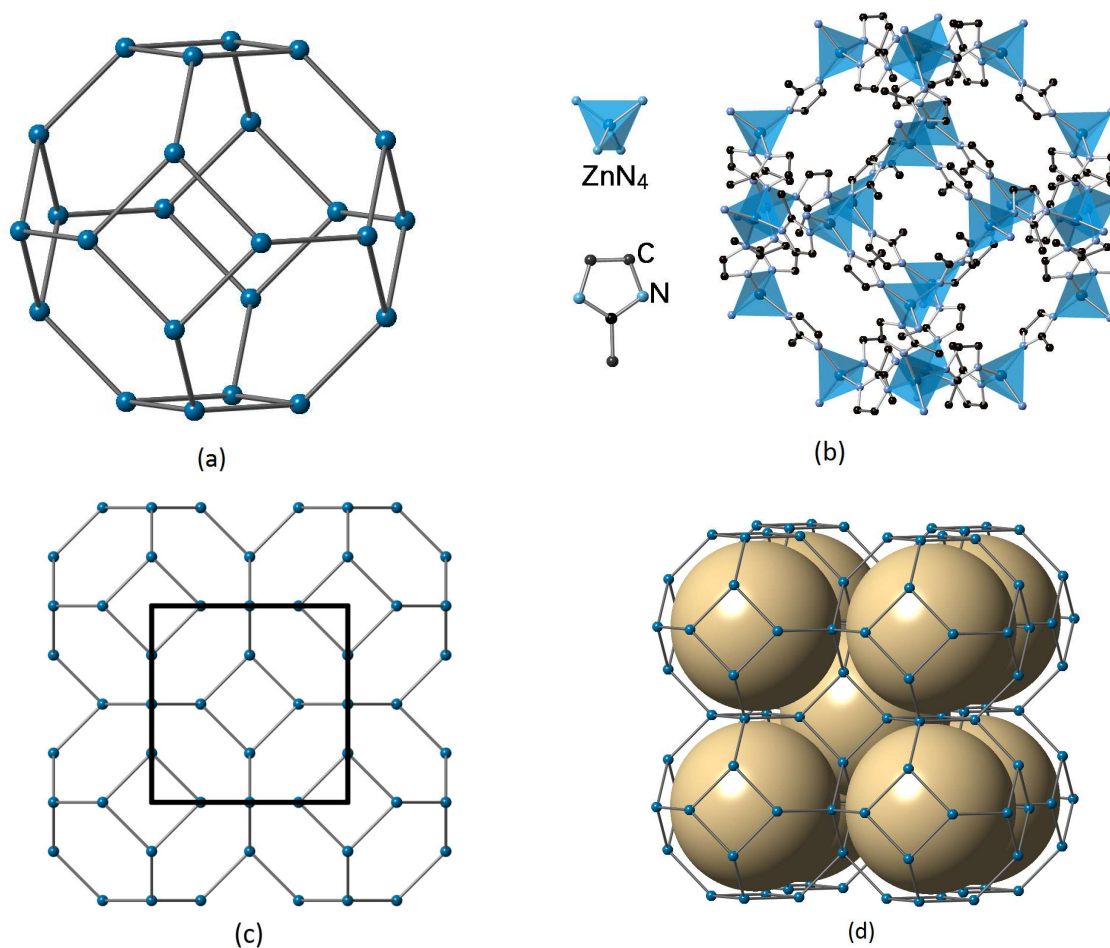


Figure 3.2 Topology of **SOD** and structure of ZIF-8

- (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

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

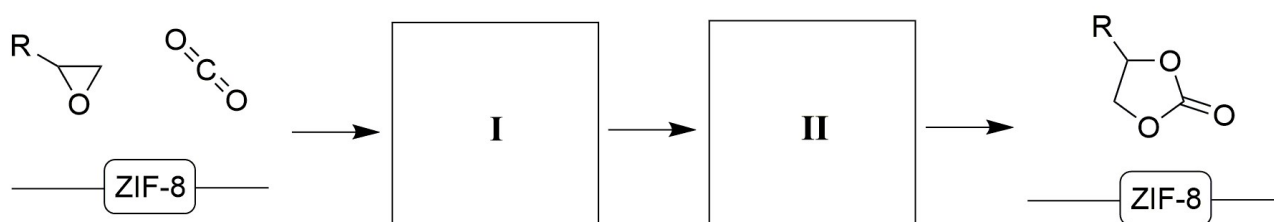
3.10 Calculate the porosity R of ZIF-8 (R is the ratio of pore volume to the actual volume of the material) and the pore volume of 1 g ZIF-8 (V_p , in cm^3).

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:



Theory

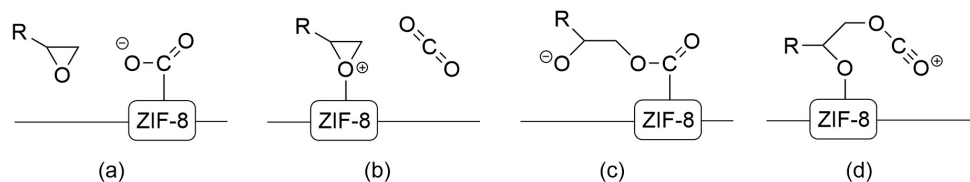


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Q3-6

English (Official)

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



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

Theory



A3-1

English (Official)

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:



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)

$$r(\text{CO}_2) = \text{_____} \text{ mmol min}^{-1}$$

3.7 (2.0 pt)

3.8 (2.0 pt)

3.9 (5.0 pt)

$$S = \text{_____} \text{m}^2$$

3.10 (7.0 pt)

$$R = \text{_____}; V_p = \text{_____} \text{cm}^3$$

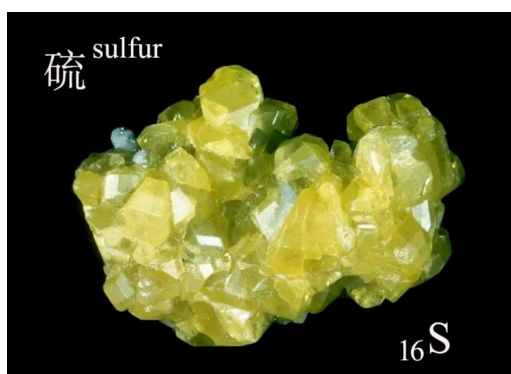
3.11 (2.0 pt)

I: ☐ (a) ☐ (b) ☐ (c) ☐ (d)
II: ☐ (a) ☐ (b) ☐ (c) ☐ (d)

3.12 (2.0 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													



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 $0.05122 \text{ mol L}^{-1}$ 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 $0.1012 \text{ mol L}^{-1}$ $\text{Na}_2\text{S}_2\text{O}_3$.

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

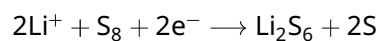
A lithium-ion battery (LIB) that possesses an average operating voltage of 3.8 V and a deliverable capacity of 3110 mAh can provide energy for a mobile phone to play videos continuously for 22 hours upon a full charge.

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

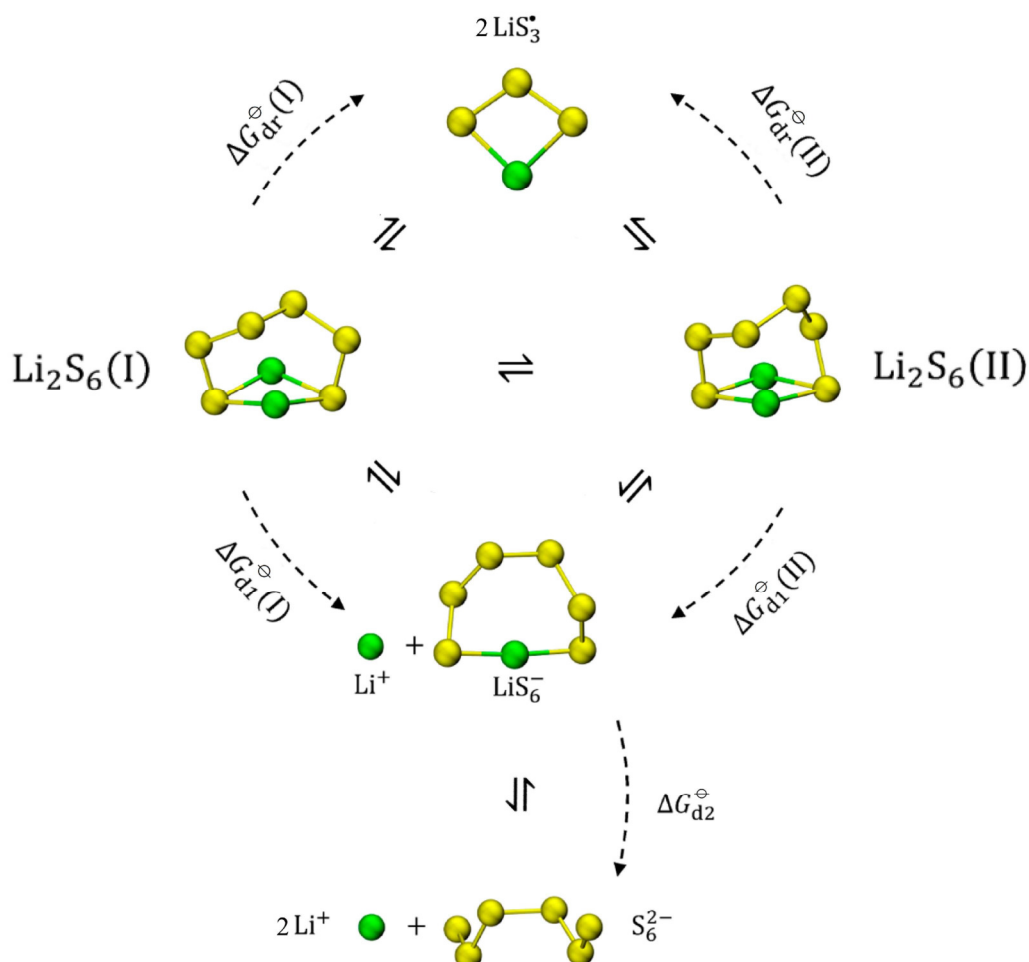
Elemental sulfur generally exist as S_8 molecules. In real lithium-sulfur batteries, S_8 is not directly reduced to Li_2S during discharge, but it undergoes stepwise reactions generating different soluble lithium polysulfides (Li_2S_n , $n = 3 - 8$). These lithium polysulfides could diffuse to the anode 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:



A theoretical study shows that two conformers with comparable energies, $\text{Li}_2\text{S}_6(\text{I})$ and $\text{Li}_2\text{S}_6(\text{II})$ 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 in DME

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

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

Theory



Q4-4

English (Official)

4.8 Using the data from **Table 4.1**, **calculate** the equilibrium concentration ratio of two conformers in DME (298.15 K, 1 bar), $\frac{[\text{Li}_2\text{S}_6(\text{II})]}{[\text{Li}_2\text{S}_6(\text{I})]}$. 4.0 pt

4.9 Using the data from **Table 4.1**, **calculate** the apparent dissociation constant of $\text{Li}_2\text{S}_6 \rightarrow \text{Li}^+ + \text{LiS}_6^-$ in DME (298.15 K, 1 bar). 5.0 pt

4.10 **Sort** the following equilibrium concentrations in decreasing order: $[\text{Li}_2\text{S}_6]$, $[\text{LiS}_6^-]$, $[\text{S}_6^{2-}]$, $[\text{LiS}_3^*]$ in DME. 4.0 pt

4.11 The standard reduction potential of metallic lithium in water at 298.15 K and 1 bar is: 6.0 pt

$$E^\ominus (\text{Li}^+/\text{Li}) = -3.040 \text{ V}$$

The standard solvation Gibbs energies of gaseous $\text{Li}^+(\text{g})$ to $\text{Li}^+(\text{sol})$ in different solvents.

	$\text{Li}^+(\text{H}_2\text{O})$	$\text{Li}^+(\text{DME})$
$\Delta G^\ominus / \text{kJ mol}^{-1}$	-116.9	-114.6

Calculate 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: $\text{S}_3^{\bullet-}$, 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:

$$[\text{S}_3^{\bullet-}] : [\text{S}_4^{2-}] : [\text{S}_5^{2-}] : [\text{S}_6^{2-}] : [\text{S}_7^{2-}] : [\text{S}_8^{2-}] = 17.50 : 1.00 : 4.50 : 55.00 : 5.00 : 0.75$$

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

Theory



A4-1

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													

4.1 (2.0 pt)

4.2 (4.0 pt)

4.3 (4.0 pt)

_____ %

Theory



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A4-2

English (Official)

4.4 (3.0 pt)

(a)

(b)

4.5 (1.0 pt)

mass ratio: _____

4.6 (5.0 pt)

_____h

Theory

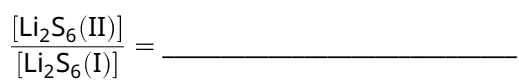


A4-3

English (Official)

4.7 (2.0 pt)

4.8 (4.0 pt)



4.9 (5.0 pt)



4.10 (4.0 pt)

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

4.11 (6.0 pt)

$E^{\ominus}(\text{Li}^+(\text{DME})/\text{Li}) = \text{_____ V}$

4.12 (5.0 pt)

$m(\text{Li}_2\text{S}) = \text{_____ mg}$

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 $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$.

Part A

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



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 $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ as a function of $[\text{NO}]$, $[\text{O}_2]$, 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 $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ as functions of M , N , A_2 and $E_{a,2}$. 4.0 pt

Theory



Q5-2

English (Official)

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 kJ 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)
$\Delta_f H_m^\ominus (\text{kJ mol}^{-1})$	91.3		33.1
$S_m^\ominus (\text{J K}^{-1} \text{ mol}^{-1})$	210.8	205.2	240.1

The standard reaction enthalpy and entropy changes of $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ 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 $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ is independent on the concentration of NO and O₂.

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

NO₂ 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 O₂. 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 NO₂ and the subsequent absorption of the formed NO₂ 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):



$$r_{S+1} = k_{S+1} [\text{O}_2] \theta_v^2 \quad r_{S-1} = k_{S-1} \theta_{\text{O}}^2$$



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



$$r_{S+3} = k_{S+3} [\text{NO}] \theta_{\text{O}}$$



$$r_{S+4} = k_{S+4} \theta_{\text{NO}_2} \quad r_{S-4} = k_{S-4} [\text{NO}_2] \theta_v$$

Assume that the adsorptions of NO, NO₂ and O (from the dissociation of O₂) 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 $\theta_v = 1 - \theta_{\text{NO}} - \theta_{\text{NO}_2} - \theta_{\text{O}}$. 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 $[\text{NO}]$, $[\text{O}_2]$, $[\text{NO}_2]$ and the rate constants involved in reactions (S1)–(S4). 6.0 pt

- 5.9** **Choose** the correct expression for the rate of $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ at the beginning of the reaction. Assume that the concentration and adsorption of NO_2 are both negligible. 4.0 pt

- (A) $r_{\text{S}+} = \frac{k_{\text{S}+3}(k_{\text{S}+1}/k_{\text{S}-1})^{0.5}[\text{NO}][\text{O}_2]^{0.5}}{1 + (k_{\text{S}+1}[\text{O}_2]/k_{\text{S}-1})^{0.5} + k_{\text{S}+2}[\text{NO}]/k_{\text{S}-2}}$
- (B) $r_{\text{S}+} = \frac{0.5k_{\text{S}+3}(k_{\text{S}+1}/k_{\text{S}-1})^{0.5}[\text{NO}][\text{O}_2]^{0.5}}{1 + (k_{\text{S}+1}[\text{O}_2]/k_{\text{S}-1})^{0.5} + k_{\text{S}+2}[\text{NO}]/k_{\text{S}-2}}$
- (C) $r_{\text{S}+} = \frac{k_{\text{S}+3}(k_{\text{S}+1}/k_{\text{S}-1})[\text{NO}][\text{O}_2]^{0.5}}{1 + k_{\text{S}+1}[\text{O}_2]/k_{\text{S}-1} + k_{\text{S}+2}[\text{NO}]/k_{\text{S}-2}}$
- (D) $r_{\text{S}+} = \frac{k_{\text{S}+4}k_{\text{S}+3}(k_{\text{S}+1}/k_{\text{S}-1})^{0.5}[\text{NO}][\text{O}_2]^{0.5}/k_{\text{S}-4}}{1 + k_{\text{S}+1}([\text{O}_2]/k_{\text{S}-1})^{0.5} + k_{\text{S}+2}[\text{NO}]/k_{\text{S}-2}}$

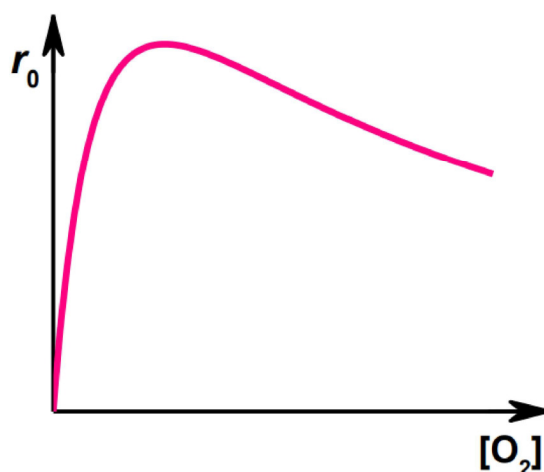
For some catalysts, the surface reaction proceeds via an alternative way instead of reaction (S3):



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

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

A catalyst (**CatY**) is used to promote the reaction of $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$. When the temperature and NO concentration are constant, the initial reaction rate changes with the concentration of O_2 as follows:



Theory



Q5-5

English (Official)

5.10 Choose a mechanism that is consistent with this curve.

6.0 pt

- (A) S3
- (B) S5
- (C) cannot be determined

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)

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

5.4 (4.0 pt)

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

5.5 (3.0 pt)

$$\Delta_r U_m^\ominus = \text{_____} \text{ kJ mol}^{-1}$$

5.6 (8.0 pt)

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

5.7 (4.0 pt)

p_{total} = _____ kPa



5.8 (6.0 pt)

$\theta_v =$ _____

5.9 (4.0 pt)

☐ (A) ☐ (B) ☐ (C) ☐ (D)

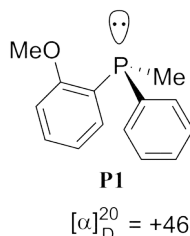
5.10 (6.0 pt)

☐ (A) ☐ (B) ☐ (C)

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								

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.

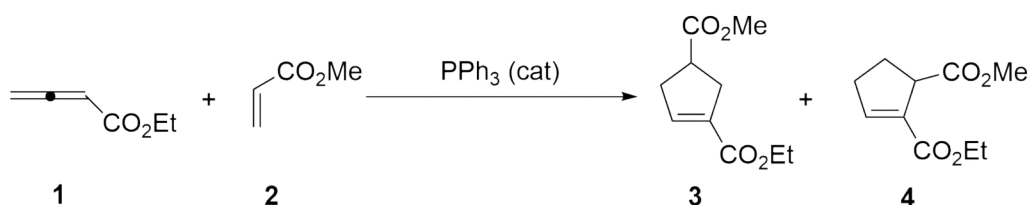


6.1 Using *R/S* symbol, assign the absolute configuration of **P1**.

3.0 pt

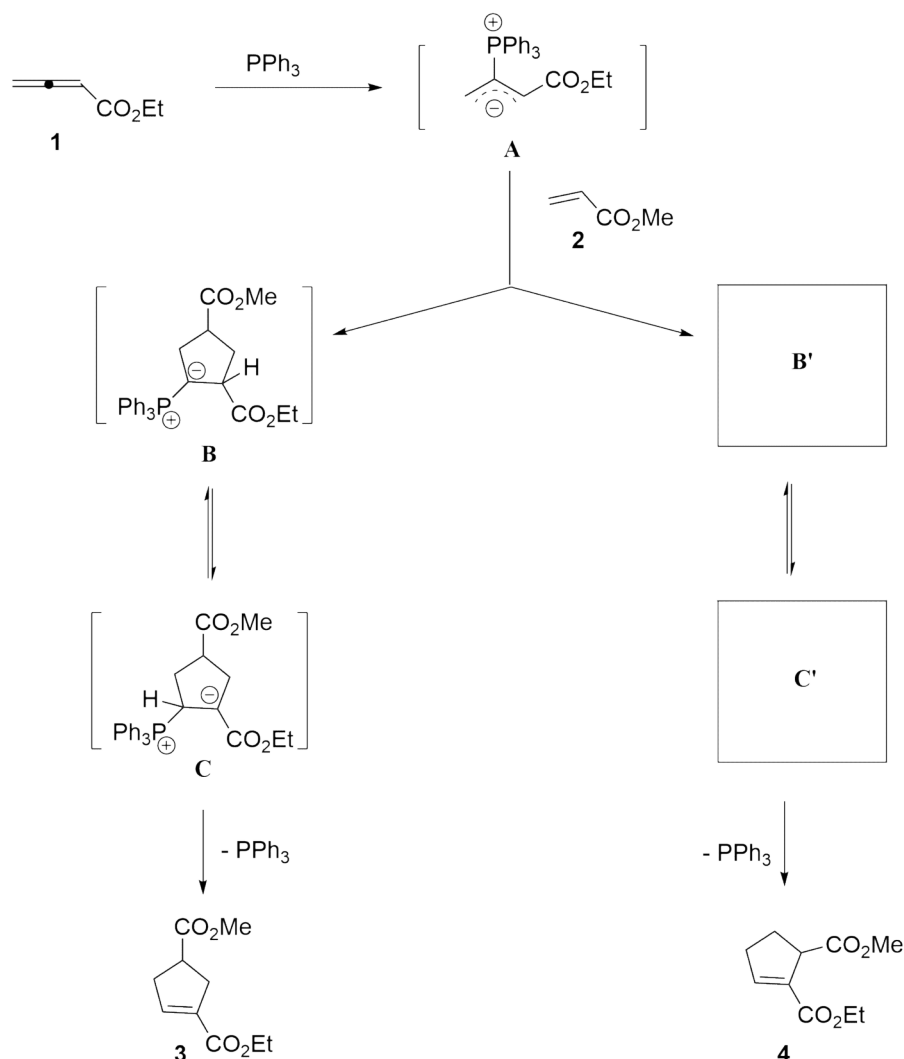
In the past two decades, as organocatalysis grew rapidly, a large number of nucleophilic phosphine-catalyzed synthetic reactions have emerged. Among them, one of the most famous phosphine-catalyzed reactions is the Lu (3+2) cycloaddition reaction, which was first developed by Chinese scientist Xiyan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

Lu (3+2) cycloaddition:



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.

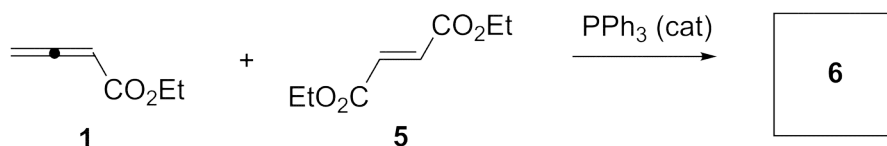
Mechanism:



- 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

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

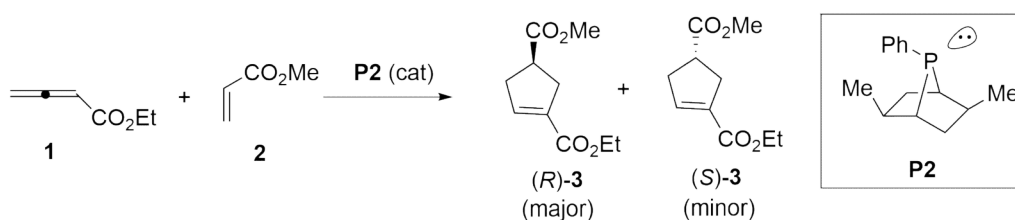
Under similar conditions, ethyl allenoate **1** and diethyl fumarate **5** readily deliver the corresponding cycloaddition product **6**.



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:

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

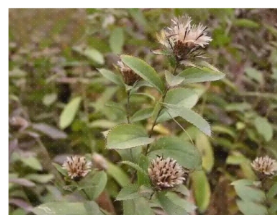
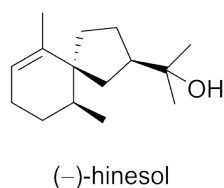
n_{major} = the amount of major enantiomer

n_{minor} = the amount of minor enantiomer

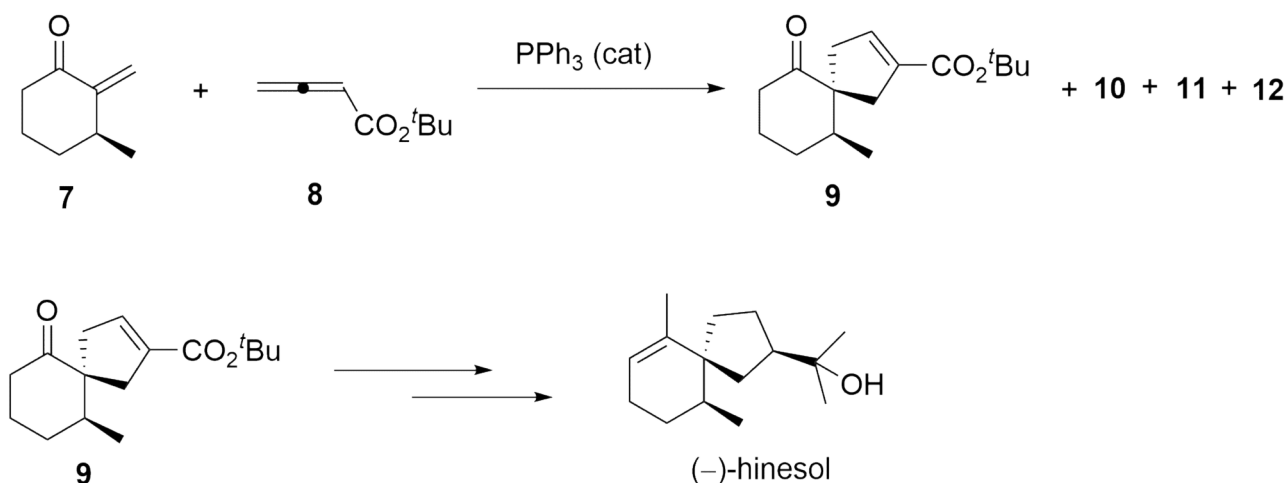
6.5 Mark the chirality centers in the chiral phosphine **P2** by using asterisks. (**Note:** 6.0 pt points will be deducted for every wrong asterisk until 0 points)

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

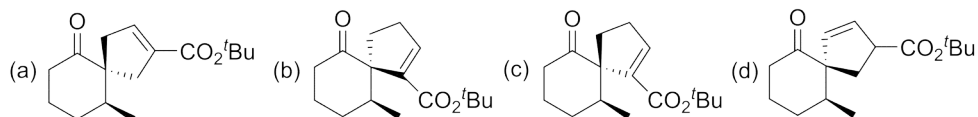
Lu (3+2) cycloaddition reaction is a versatile tool in organic synthesis. For example, it was successfully used to synthesize (–)-hinesol, an important component of the Chinese medicinal herb Chang Zhu (*Atractylodes lancea* var *Chinensis*). Under the catalysis of PPh_3 , a chiral cyclohexanone **7** 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.



Chang Zhu



6.7 In the following compounds, **choose** 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)

Theory



A6-2

English (Official)

6.3 (8.0 pt)

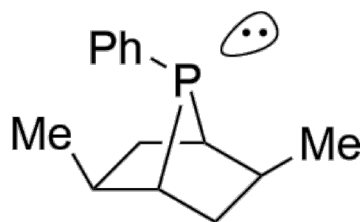
B' (4.0 pt)

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)

Organic Molecules in Life

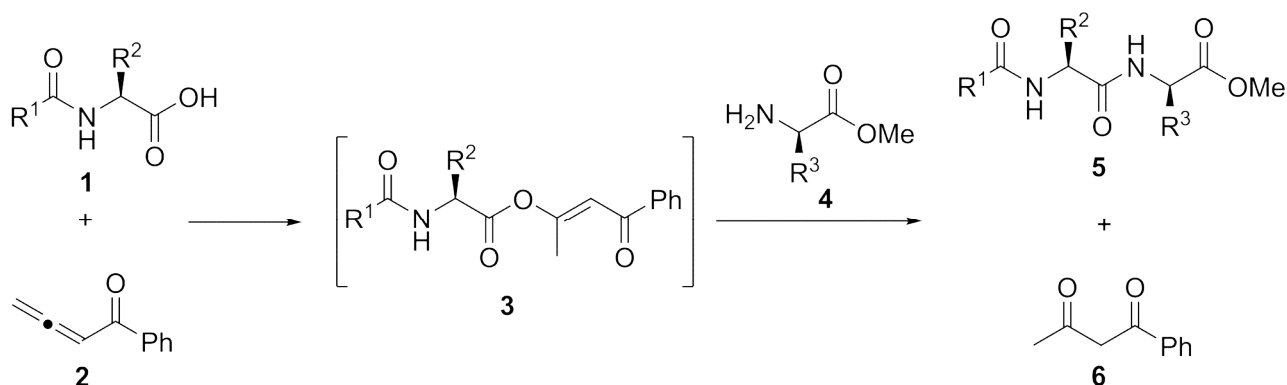
9% of the total				
Question	7.1	7.2	7.3	Total
Points	12	8	12	32
Score				

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.

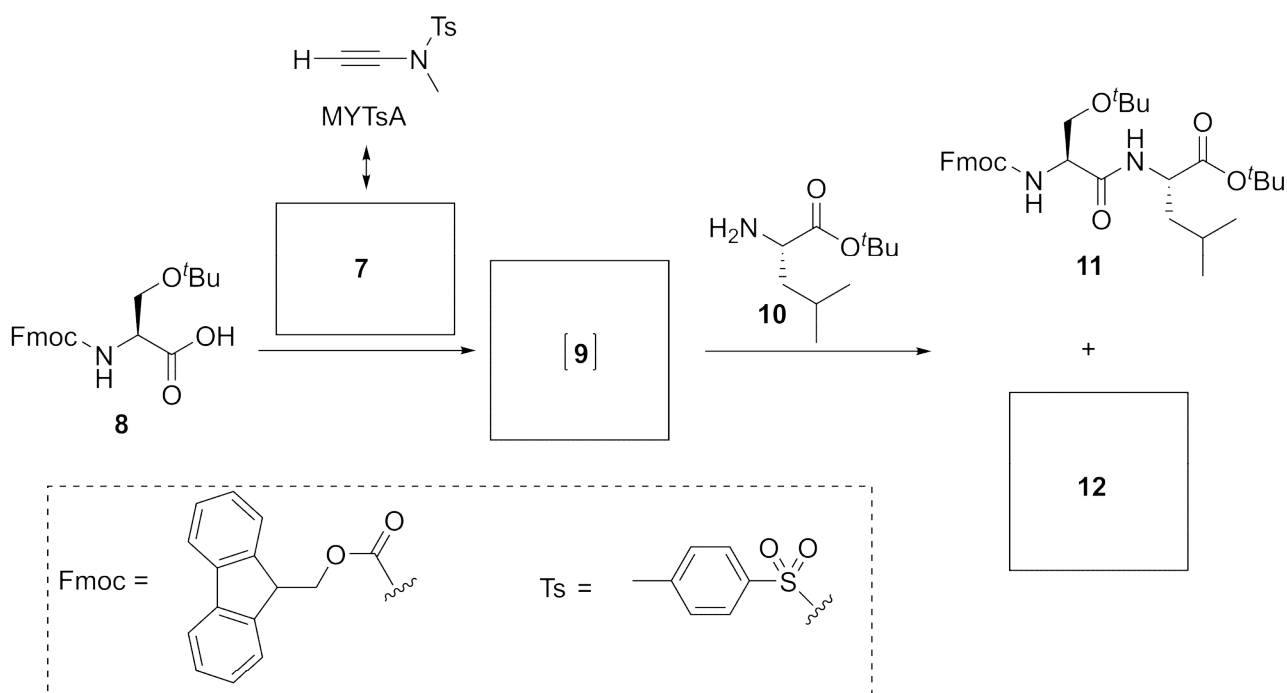


Stamp issued on the 50th anniversary (2015) of the first synthesis of crystalline bovine insulin

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**.



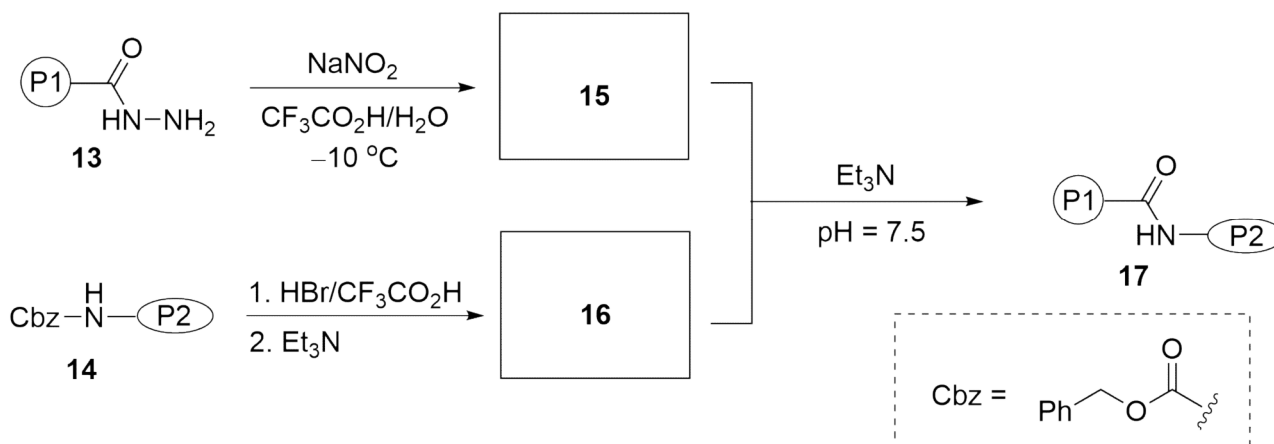
Similarly, *N*-ethynyl-*N*-methyl-*p*-toluenesulfonamide (MYTsA) with its major resonance structure **7** (involvement of Ts group is not considered) can activate carboxylic acid in the same way as allenone **2**.



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.

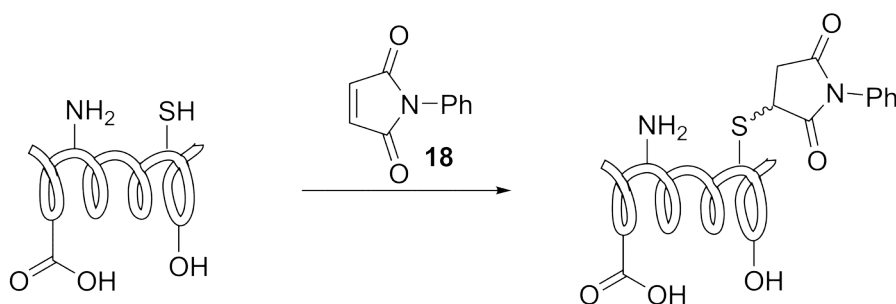


Note: P1, P2 = peptides

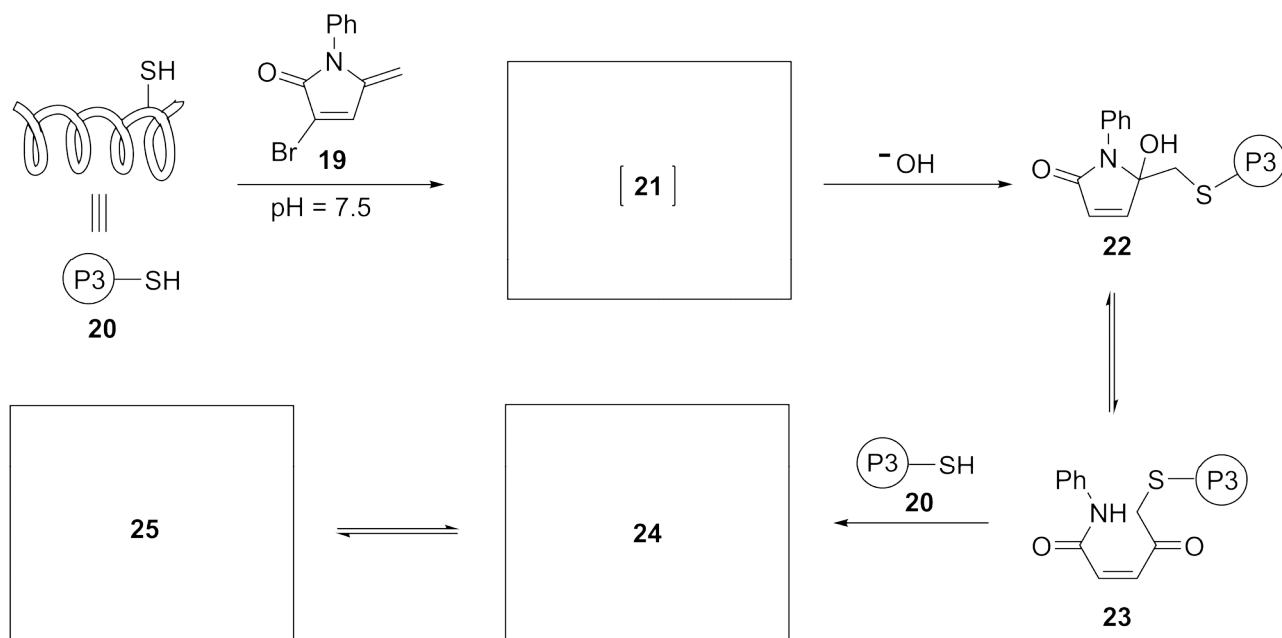
7.2 Draw the structures of compounds **15** and **16**.

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**.



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

Theory



A7-1

English (Official)

Organic Molecules in Life

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

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)

Theory



A7-2

English (Official)

7.3 (12.0 pt)

21 (4.0 pt)

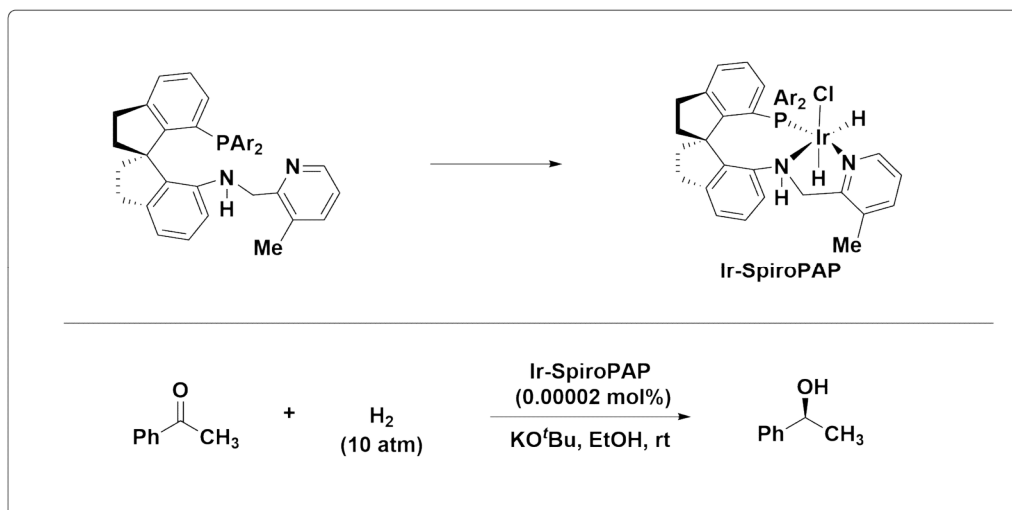
24 (4.0 pt)

25 (4.0 pt)

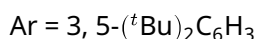
Amazing Chiral Spiro Catalyst

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									

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:



Part A

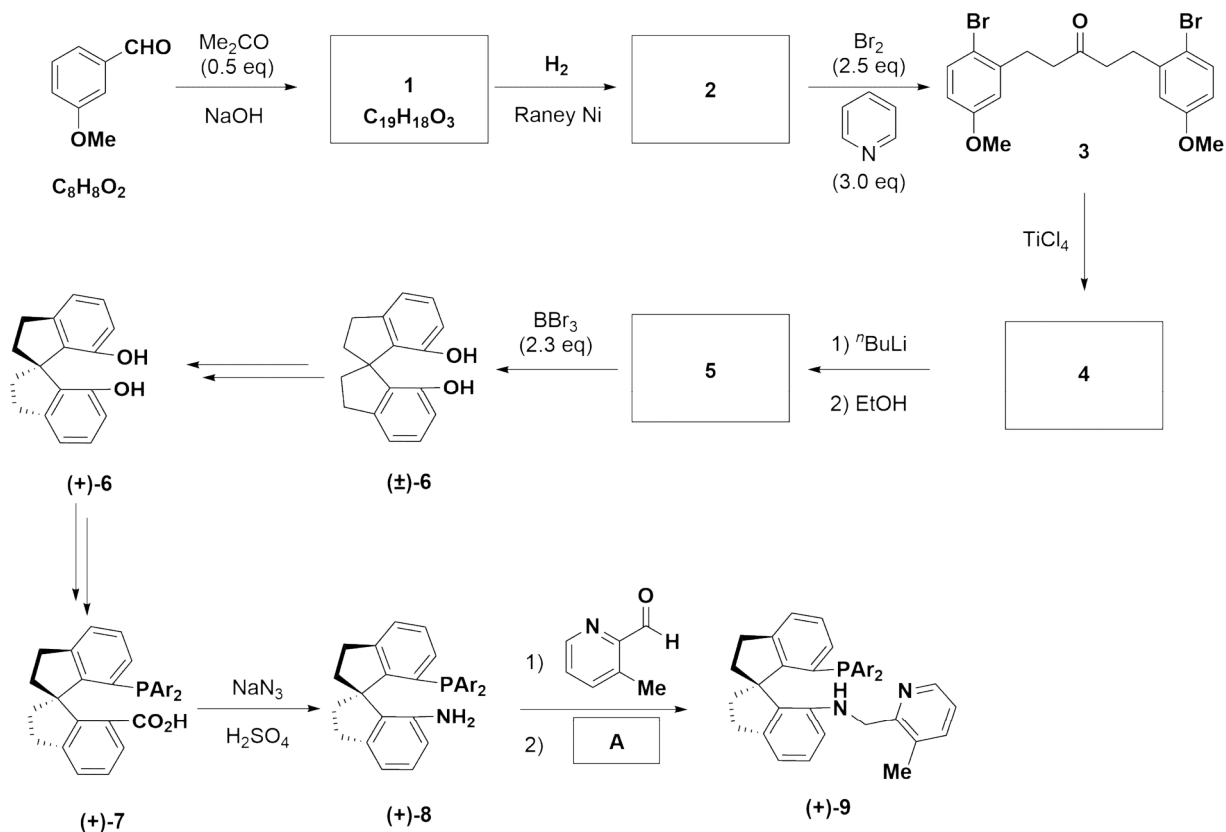
The synthetic route of the chiral ligand SpiroPAP is shown in the following scheme.

Theory



Q8-2

English (Official)



Note:

eq = equivalent

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

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

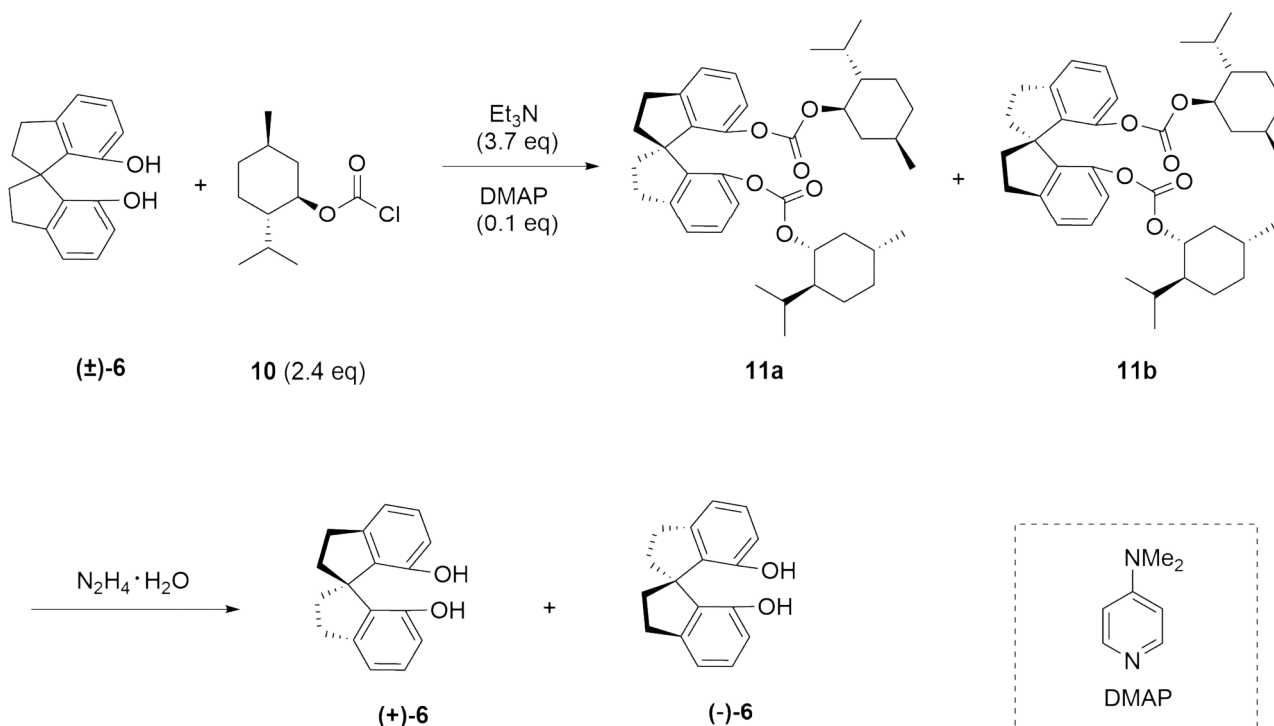
16.0 pt

8.2 From the following reagents, which reagent **A** can **NOT** be used for the transformation of **8** to **9**?

2.0 pt

- (a) $\text{NaBH}(\text{OAc})_3$
- (b) NaBH_3CN
- (c) NH_2NH_2 , NaOH
- (d) NaBH_4

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**.



Note:

eq = equivalent

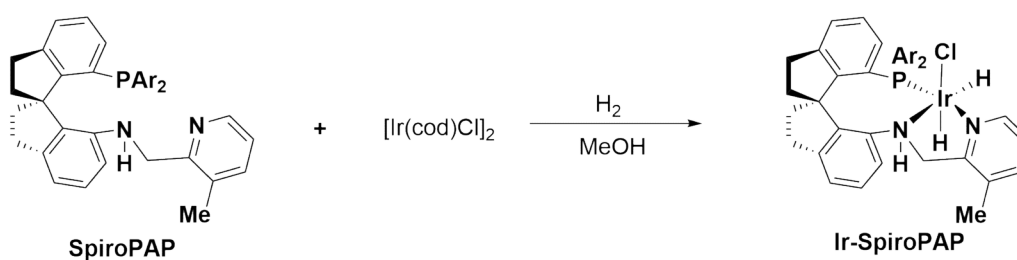
8.3 **Choose** the correct statement below.

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 $[\text{Ir}(\text{cod})\text{Cl}]_2$ (cod is cycloocta-1,5-diene) in MeOH under hydrogen as shown below.



Note:

Ar = 3, 5-(^tBu)₂C₆H₃

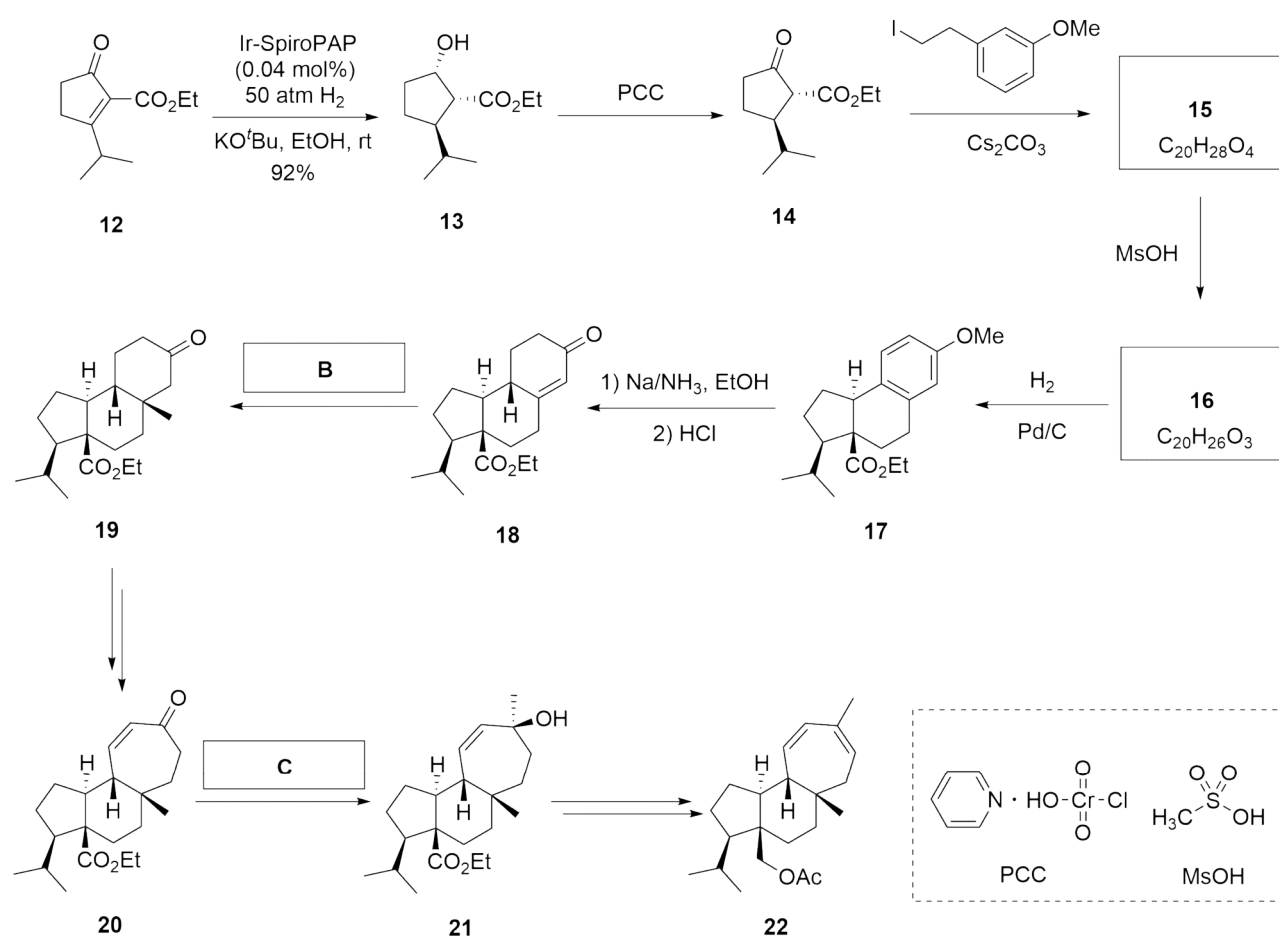
8.4 Write the oxidation number of Ir in the catalyst Ir-SpiroPAP.

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

Theory



Q8-5

English (Official)

- 8.7** From the following reagents, **choose** the best for **B**. 2.0 pt
- (a) MeLi/CeCl₃
 - (b) MeLi/CuI
 - (c) MePh₃P⁺I⁻, ⁿBuLi
 - (d) Me₃S⁺I⁻, NaH

- 8.8** From the following reagents, **choose** the best for **C**. 2.0 pt
- (a) MeLi/CeCl₃
 - (b) MeLi/CuI
 - (c) MePh₃P⁺I⁻, ⁿBuLi
 - (d) Me₃S⁺I⁻, NaH

Theory



A8-1

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									

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)

Theory



A8-2

English (Official)

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)

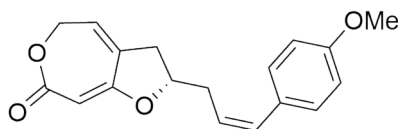
Total Synthesis of Capitulactone

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.

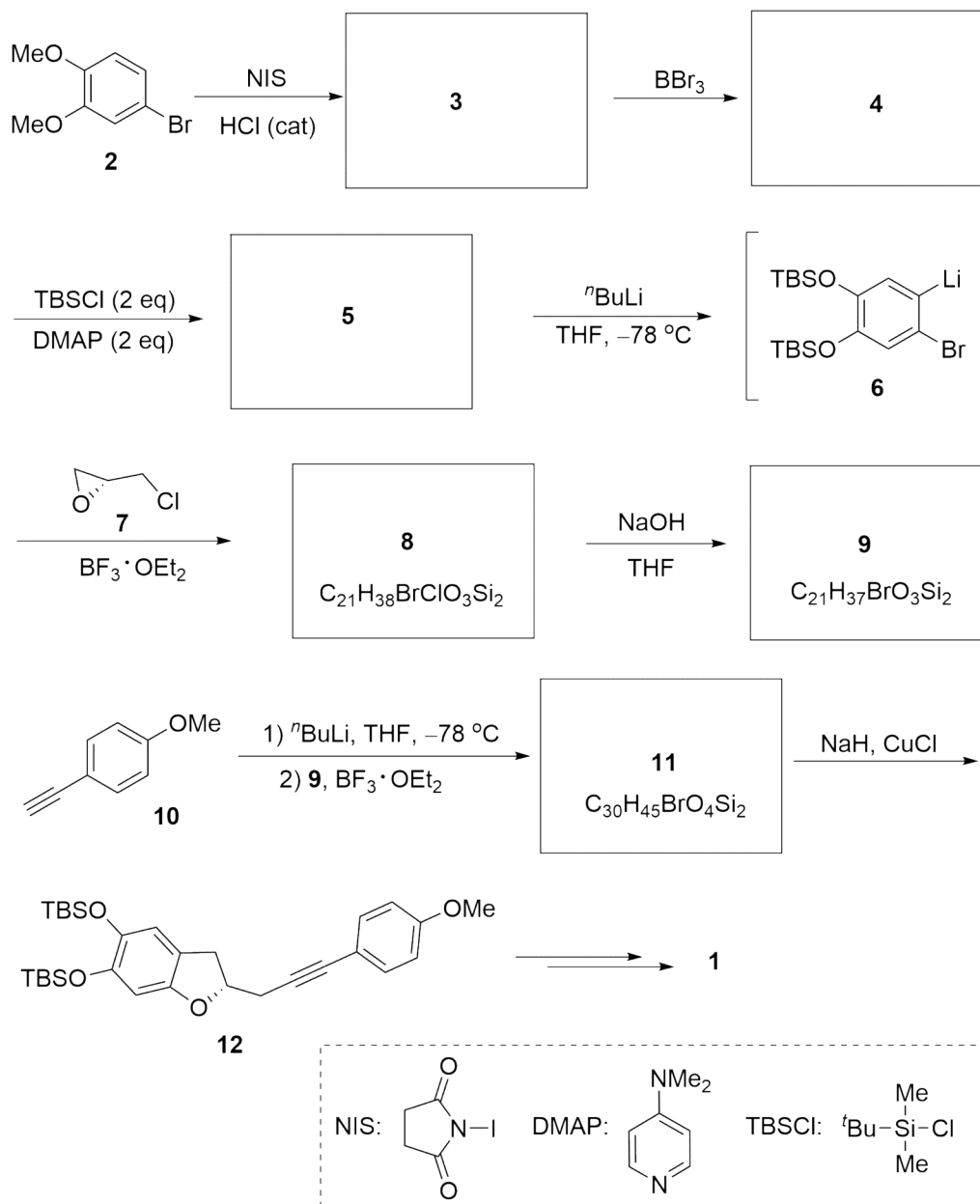


Curculigo capitulata



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.

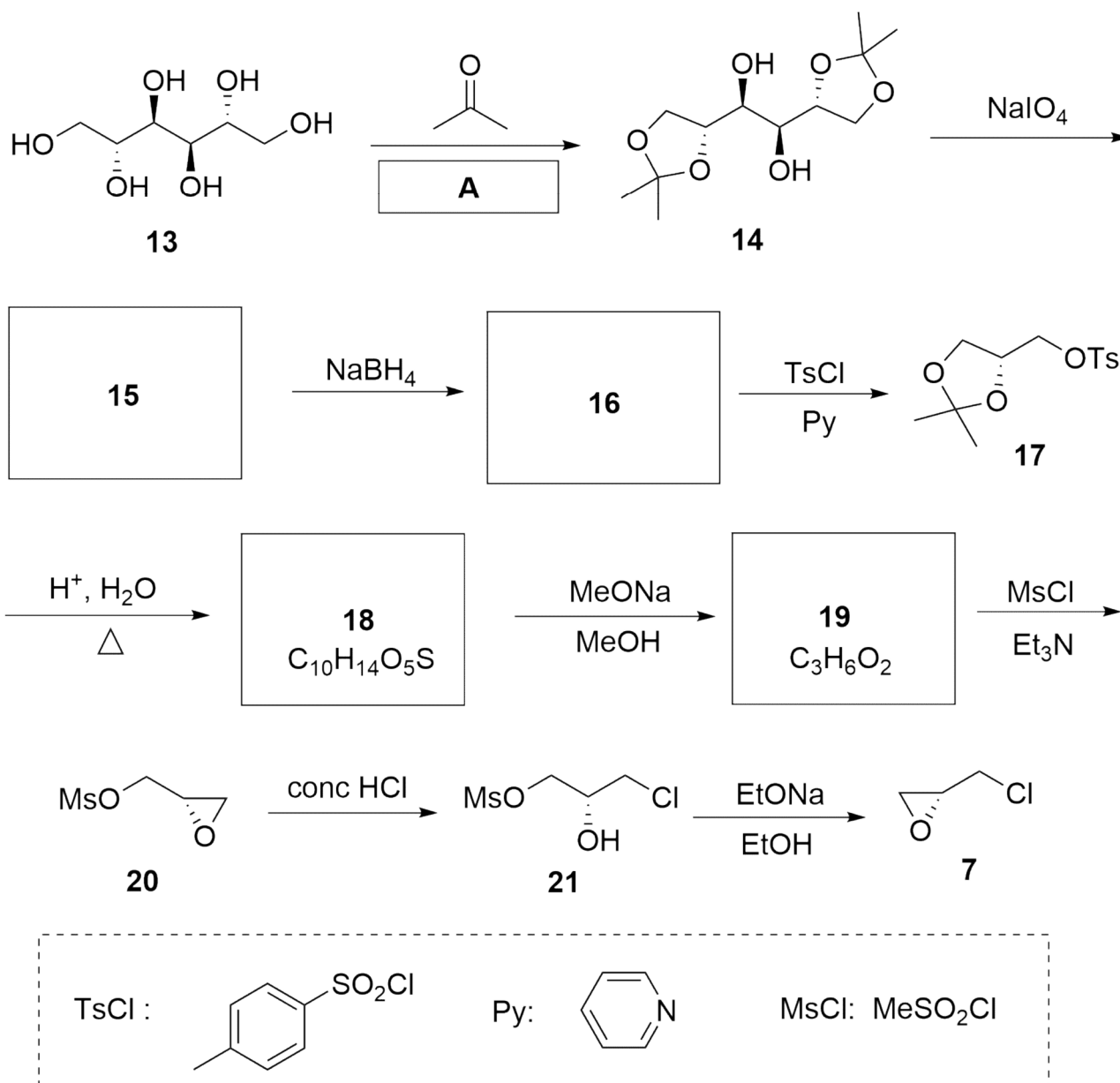
**Note:**

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

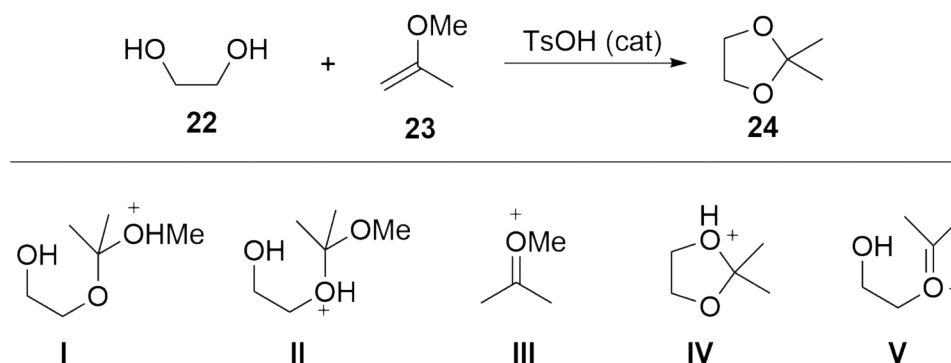
conc = concentrated

9.2 From the following conditions, **choose** the best for **A**. 2.0 pt

- (a) Pyridine
- (b) 5% KOH/H₂O
- (c) 1% HCl/H₂O
- (d) Anhydrous ZnCl₂

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 toluenesulfonic 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. 2.0 pt

- (a) **I, II, III, IV, V**
- (b) **III, II, I, V, IV**
- (c) **III, I, II, IV, V**
- (d) **III, I, II, V, IV**

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)

Theory



A9-2

English (Official)

9.1 (cont.)

9 (4.0 pt)

11(4.0 pt)

9.2 (2.0 pt)

☐ (a)

☐ (b)

☐ (c)

☐ (d)

Theory



54th IChO2022
International Chemistry Olympiad
TIANJIN, CHINA

A9-3

English (Official)

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)