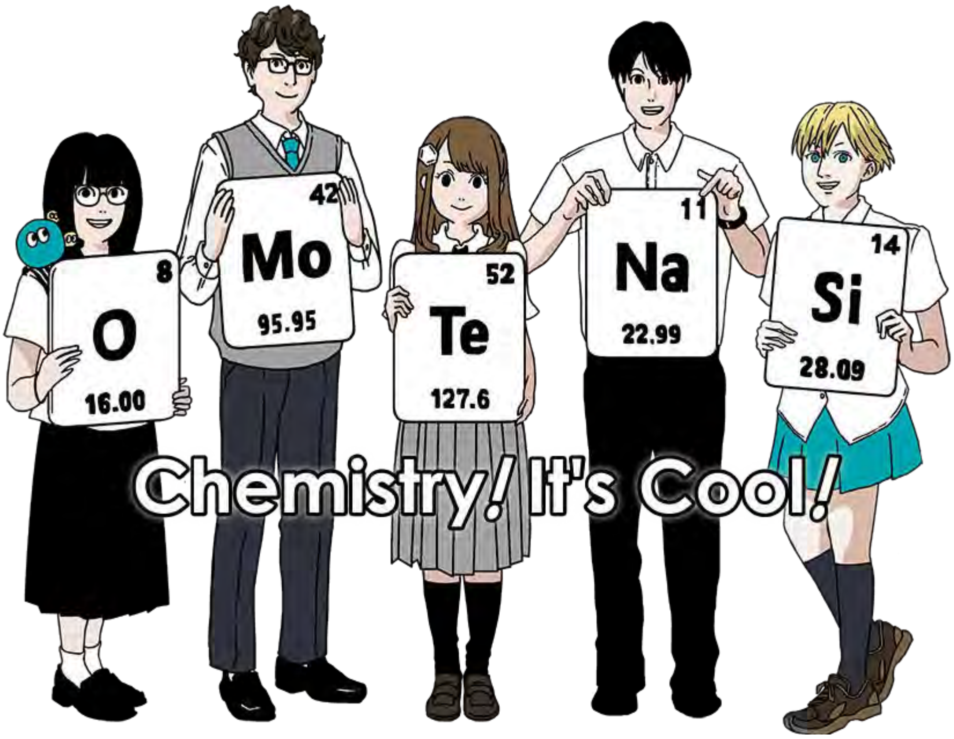
International Chemistry Olympiad 2021 Japan
53rd IChO2021 Japan
25th July – 2nd August, 2021
https://www.icho2021.org



Preparatory Problems

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Preface

We are very pleased to introduce the Preparatory Problems for the 53rd International Chemistry Olympiad. These problems cover a wide range of challenging and important topics in modern chemistry. We hope that both students and their mentors will enjoy solving these problems and prepare for the Olympics. The problems include 6 topics of advanced difficulty for the Theoretical part and 3 topics of advanced difficulty for the Practical part, in addition to the subjects normally covered in high school chemistry courses. These topics are explicitly listed under "Fields of Advanced Difficulty" and their applications are shown in the preparatory problems consisting of 31 theoretical problems and 6 practical tasks. The solutions will be emailed to the head mentor of each country by February, 2021 and will be published online in July, 2021. We welcome any comments, corrections and questions about the problems via email to: preparatory@icho2021.org.

The International Chemistry Olympiad is a great opportunity for young people from all over the world to deepen their understanding of the wonders of chemistry, and inspire each other. At the same time, it is a wonderful opportunity to make friends around the world, and enjoy the history and culture of the host country. COVID-19 is widespread all over the world and the situation is very severe, but we hope that we can meet you in Osaka, Japan in July.

Acknowledgement

We would like to express our deepest gratitude to all the authors for their great efforts in creating both preparatory and competition problems. We would also like to thank the reviewers for their valuable comments and suggestions.

Appendix

The preparatory problems are published to help the students and the mentors prepare for the usual real IChO including the theoretical problems and the practical tasks. However, because of the pandemic of COVID-19, the Organizing Committee finally decided to hold the IChO2021 Japan as the remote IChO to ensure the safety of the participants. Since the practical tasks will not be conducted in the remote IChO2021, the practical tasks in the preparatory problems are out of use for the IChO2021. It is not necessary for the students who want to participate the IChO2021 to study and/or examine the practical tasks and the advanced skills included in the preparatory problems.

Instead of the deletion of the practical tasks from the preparatory problems, however, we moved them to the Appendix part. Even though the practical tasks will not be conducted in IChO2021, the importance of laboratory experiments does not change in the chemistry. We hope to have any opportunity where the practical tasks prepared for the IChO2021 Japan are fully utilized. The practical tasks included in the Appendix part will help such an event.

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Theoretical Problems

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Fields of Advanced Difficulty: Theoretical subject

Structure and characterization of inorganic compound:

- solid state structure, unit cell, crystal field theory, a concept of hole.

Quantum mechanical behavior of molecules:

- molecular vibration, how to read potential energy surface, definition of entropy based on Boltzmann's principle.

Thermodynamics and kinetics:

- relationship between electrode potential and Gibbs free energy, adsorption isotherm.

Stereochemistry:

- conformation of fused bi- or tri-cyclic alkanes, chirality, stereospecific reaction, stereoselectivity by steric hindrance, axial attack in cyclohexane system.

Number of signals in NMR (^{1}H, ^{13}C, and heteronuclear NMR) and chemical shift in ^{1}H NMR.

Reactive intermediate and species:

- carbenoid, non-benzenoid aromatics, organic main group-metal compounds, heteroatom–heteroatom bonds.

Notes

Students are not expected to cover the following advanced topics:

Pericyclic reaction other than Diels-Alder reaction, Conservation of orbital symmetry, Polymer chemistry, Phase equilibrium, Catalytic reaction on surface, Normal modes of molecular vibration, Molecular orbital method, Distribution function, Slater rule.

The practical tasks in the Appendix part include the following advanced skills, although the practical examination will not be conducted in the IChO2021 Japan:

Preparation technique:

- vacuum filtration following the described procedure.

Purification:

- recrystallization and column chromatography following the described procedure.

Physical Constants and Equations

Constants

Speed of light in vacuum, $c = 2.99792458 \times 10^{8}$ m s^{-1}

Planck constant, $h = 6.62607015 \times 10^{-34}$ J s

Elementary charge, $e = 1.602176634 \times 10^{-19}$ C

Electron mass, $m_e = 9.10938370 \times 10^{-31}$ kg

Electric constant (permittivity of vacuum), $\varepsilon_0 = 8.85418781 \times 10^{-12}$ F m^{-1}

Avogadro constant, $N_A = 6.02214076 \times 10^{23}$ mol^{-1}

Boltzmann constant, $k_B = 1.380649 \times 10^{-23}$ J K^{-1}

Faraday constant, $F = N_A \times e = 9.64853321233100184 \times 10^{4}$ C mol^{-1}

Gas constant, $R = N_A \times k_B = 8.31446261815324$ J K^{-1} mol^{-1}
$= 8.2057366081 \times 10^{-2}$ L atm K^{-1} mol^{-1}

Unified atomic mass unit, $u = 1$ Da $= 1.66053907 \times 10^{-27}$ kg

Standard pressure, $p = 1$ bar $= 10^{5}$ Pa

Atmospheric pressure, $p_{atm} = 1.01325 \times 10^{5}$ Pa

Zero degree Celsius, 0 °C = 273.15 K

Ångström, 1 Å = 10^{-10} m

Picometer, 1 pm = 10^{-12} m

Electronvolt, 1 eV = $1.602176634 \times 10^{-19}$ J

Part-per-million, 1 ppm = 10^{-6}

Part-per-billion, 1 ppb = 10^{-9}

Part-per-trillion, 1 ppt = 10^{-12}

pi, $\pi = 3.141592653589793$

The base of the natural logarithm (Euler's number), $e = 2.718281828459045$

Equations

The ideal gas law: $PV = nRT$

, where P is the pressure, V is the volume, n is the amount of substance, T is the absolute temperature of ideal gas.

The first law of thermodynamics: $\Delta U = q + w$

, where ΔU is the change in the internal energy, q is the heat supplied, w is the work done.

Enthalpy H: $H = U + PV$

Entropy based on Boltzmann's principle S: $S = k_B \ln W$

, where W is the number of microstates.

The change of entropy ΔS:

$$\Delta S = \frac{q_{rev}}{T}$$

, where q_{rev} is the heat for the reversible process.

Gibbs free energy G: $G = H - TS$

$\Delta_r G^0 = -RT \ln K = -zFE^0$

, where K is the equilibrium constant, z is the number of electrons, E^0 is the standard electrode potential.

Reaction quotient Q: $\Delta_r G = \Delta_r G^0 + RT \ln Q$

For a reaction

$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

, where [A] is the concentration of A.

Heat change Δq: $\Delta q = nc_{\mathrm{m}}\Delta T$

, where c_{m} is the temperature-independent molar heat capacity.

Nernst equation for redox reaction:

$$E = E^0 + \frac{RT}{zF} \ln\left(\frac{C_{\mathrm{ox}}}{C_{\mathrm{red}}}\right)$$

, where C_{ox} is the concentration of oxidized substance, C_{red} is the concentration of reduced substance.

Arrhenius equation:	$k = A \exp\left(-\frac{E_a}{RT}\right)$, where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy. $\exp(x) = e^x$
Lambert–Beer equation:	$A = \varepsilon l c$, where A is the absorbance, ε is the molar absorption coefficient, l is the optical path length, c is the concentration of the solution.
Henderson−Hasselbalch equation:	For an equilibrium $\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$, where equilibrium constant is K_a, $\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$
Energy of a photon:	$E = h\nu = h\frac{c}{\lambda}$, where ν is the frequency, λ is the wavelength of the light.
The sum of a geometric series:	When $x \neq 1$, $1 + x + x^2 + \dots + x^n = \sum_{i=0}^{n} x^i = \frac{1 - x^{n+1}}{1 - x}$
Approximation equation that can be used to solve problems:	When $x \ll 1$, $\frac{1}{1 - x} \sim 1 + x$

Periodic table

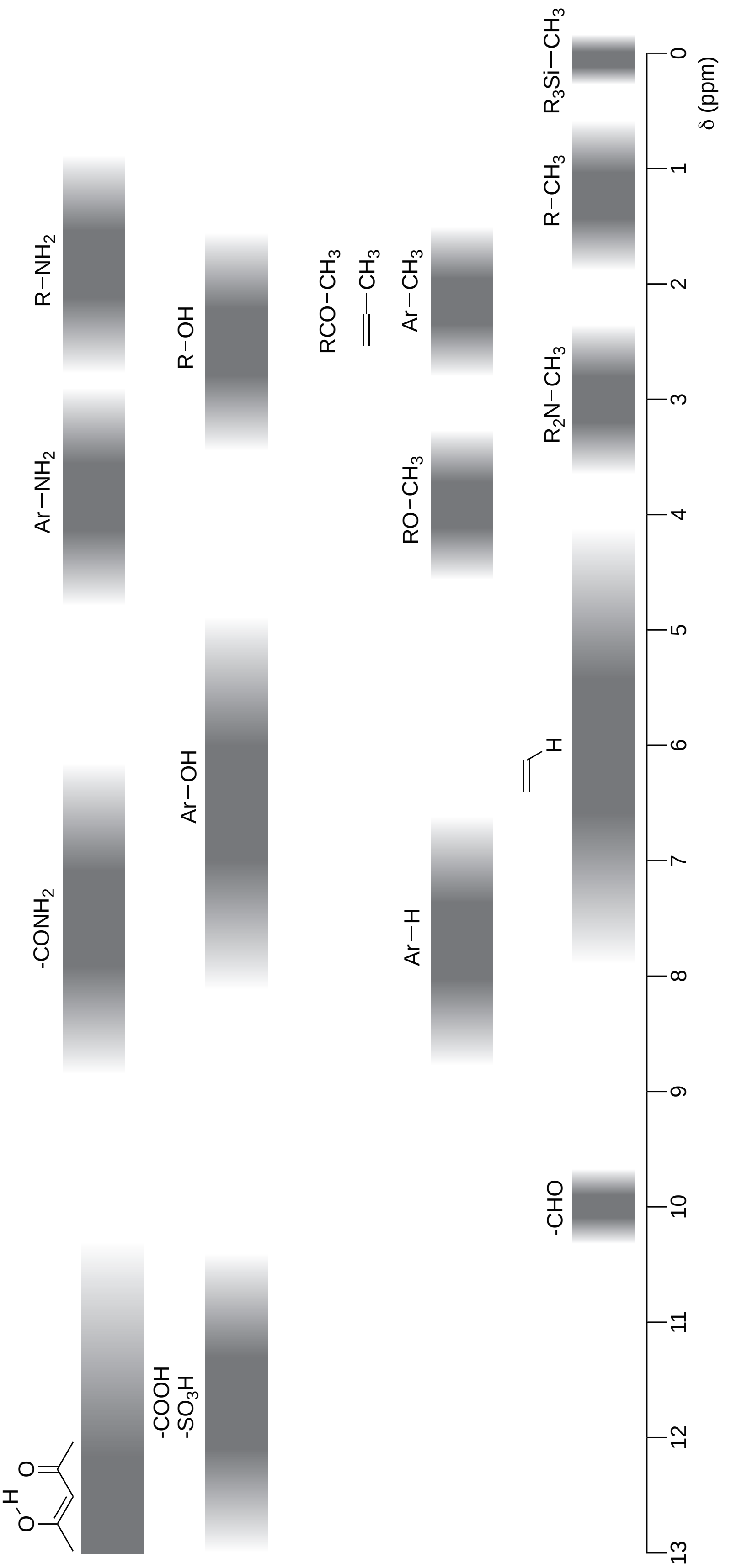
Key:

113 Nh Nihonium [278]	atomic number Symbol name atomic weight [in parenthesis for the radioactive element]

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.00798																	2 He Helium 4.002602
3 Li Lithium 6.968	4 Be Beryllium 9.012183											5 B Boron 10.814	6 C Carbon 12.0106	7 N Nitrogen 14.00686	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989769	12 Mg Magnesium 24.306											13 Al Aluminium 26.981539	14 Si Silicon 28.085	15 P Phosphorus 30.973762	16 S Sulfur 32.068	17 Cl Chlorine 35.452	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium [99]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293
55 Cs Caesium 132.905452	56 Ba Barium 137.327	57-71 La-Lu Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.384	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium [210]	85 At Astatine [210]	86 Rn Radon [222]
87 Fr Francium [223]	88 Ra Radium [226]	89-103 Ac-Lr Actinoids	104 Rf Rutherfordium [267]	105 Db Dubnium [268]	106 Sg Seaborgium [271]	107 Bh Bohrium [272]	108 Hs Hassium [277]	109 Mt Meitnerium [276]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [278]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [293]	118 Og Oganesson [294]

57-71 La-Lu Lanthanoids :	57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90766	60 Nd Neodymium 144.242	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668
89-103 Ac-Lr Actinoids :	89 Ac Actinium [227]	90 Th Thorium 232.0377	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium [237]	94 Pu Plutonium [239]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [252]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [262]

^1H NMR Chemical Shifts



Δδ for one alkyl group-substitution: *ca*. +0.4 ppm

Safety

Participants in the Olympiad must be prepared to work in a chemical laboratory and be aware of all relevant rules and safety procedures. The organizers will strictly enforce the safety rules given in Appendix A of the IChO Regulations during the Olympiad.

The Preparatory Problems are designed to be carried out in properly equipped chemical laboratories under competent supervision **only**. We did not include specific and detailed safety and disposal instructions as regulations are different in each country. Mentors must carefully adapt the problems accordingly.

The GHS hazard statements (H-phrases) associated with the materials used are indicated in the problems. Their meanings are as follows:

Physical Hazards

H225	Highly flammable liquid and vapor.
H226	Flammable liquid and vapor.
H227	Flammable liquid.
H228	Flammable solid.
H271	May cause fire or explosion; strong oxidizer.
H272	May intensify fire; oxidizer.
H290	May be corrosive to metals.

Health Hazards

H301	Toxic if swallowed.
H302	Harmful if swallowed.
H303	Maybe harmful if swallowed.
H304	May be fatal if swallowed and enters airways.
H305	May be harmful if swallowed and enters airways.
H311	Toxic in contact with skin.
H312	Harmful in contact with skin.
H313	May be harmful in contact with skin.
H314	Causes severe skin burns and eye damage.
H315	Causes skin irritation.
H316	Causes mild skin irritation.
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage.
H319	Causes serious eye irritation.
H320	Causes eye irritation.
H331	Toxic if inhaled.
H332	Harmful if inhaled.
H333	May be harmful if inhaled.
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H335	May cause respiratory irritation.
H336	May cause drowsiness or dizziness.
H351	Suspected of causing cancer.
H361	Suspected of damaging fertility or the unborn child.
H361d	Suspected of damaging the unborn child.
H361f	Suspected of damaging fertility.
H362	May cause harm to breast-fed children.
H370	Causes damage to organs.

H371	May cause damage to organs.
H372	Causes damage to organs through prolonged or repeated exposure.
H373	May cause damage to organs through prolonged or repeated exposure.

Environmental Hazards

H400	Very toxic to aquatic life.
H401	Toxic to aquatic life.
H402	Harmful to aquatic life.
H410	Very toxic to aquatic life with long lasting effects.
H411	Toxic to aquatic life with long lasting effects.
H412	Harmful to aquatic life with long lasting effects.
H413	May cause long-lasting harmful effects to aquatic life.

Chemicals or substrates with GHS hazard statement H300, H310, H330, H340, H350, and H360 are not allowed to be used in IChO and according activities.

Problem 1. Revision of SI unit

The definitions of the SI base units were fully revised on May 20, 2019. Let us examine some of the definitions related to chemistry.

Part 1.

Before the new definition, the Avogadro number, N_A, was defined as 'the number of atoms contained in 0.012 kg of the carbon isotope ^{12}C'. In other words, a collection of N_A atoms of ^{12}C has a mass of 0.012 kg.

To determine N_A experimentally, 0.012 kg of ^{12}C must be accurately measured, which requires a weight 'standard'. Traditionally, the kilogram prototype has served this purpose.

In practice, an international research consortium consisting of eight institutes including a Japanese one made a single crystal of silicon (Si) composed solely of ^{28}Si, from which a true sphere was cut for the determination of N_A. The single crystal of Si has a diamond-type crystal system with the cubic unit cell as shown in Figure 1.

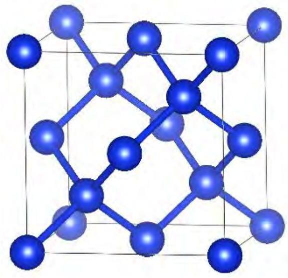


Figure 1. Single crystal of Si.

1-1. **Determine** the number of atoms of Si, n, involved in the unit cell.

Let us consider the density of the true sphere of the single crystal of Si. The length of each side of the unit cell is a [m]. The atomic mass of ^{28}Si is m = 28.09 u, where u is defined in the former fashion as:

$$u = \frac{1\times10^{-3}}{N_A}\ \text{[kg]}$$

which has the same meaning as the atomic mass unit Dalton (Da).

1-2. **Write** an equation for the density, d [kg m^{-3}], using n, m, and a.

The radius, r, of the true sphere of Si was measured to be r = 4.69 cm. Using the kilogram prototype, the mass of the sphere was determined to be w = 1.00 kg. The lattice length of the unit cell was determined to be a = 5.43 Å by an X-ray diffraction analysis.

1-3. **Calculate** the Avogadro number, N_A, using the measured parameters with three significant figures.

Part 2.

In the new definition, N_A is defined with a finite number of digits (Table 1). In this situation, a collection of N_A atoms of ^{12}C does not exactly have a mass of 0.012 kg.

The new definition enables calculating mass using the equation found in Q1-3. In fact, mass can now be determined without using the kilogram prototype if the volume is accurately measured. The kilogram prototype itself is not easy to access, and replicas are also not easily available worldwide. In addition, the aging of the prototype cannot be ignored. Determining mass without using the prototype has therefore a significant merit. As a result, seven fundamentally important constants have been determined using the newest measurement data based on the consensus of multiple research institutes.

Three of these constants are presented in **Table 1**.

Table 1. Three re-defined constants

Constant	Notation	Newly defined value	Unit
Avogadro constant	N_A	$6.02214076 \times 10^{23}$	mol^{-1}
Planck constant	h	$6.62607015 \times 10^{-34}$	J s
Velocity of light	c	2.99792458×10^{8}	$m\ s^{-1}$

Here, the product of the Avogadro and Planck constants is theoretically also a constant.

2-1. Based on these facts, **select** all the appropriate options for the determination of mass.
To determine mass:

□ N_A alone is sufficient □both N_A and h are required □h alone is sufficient

Let us define mass by considering the units of the constants. The Avogadro constant has the unit mol^{-1}. Since this unit has no apparent unit of mass, discussion of mass based on this constant would be difficult. On the other hand, the unit of the Planck constant, J s, can be rewritten as kg $m^2\ s^{-1}$, which seems more suitable for obtaining a definition of mass. To use this approach, we must understand the definitions of 1 s of time and 1 m of distance.

In the new definitions of the SI units, 1 s is based on the experimental observation that the energy difference of the hyperfine energy splitting of ^{133}Cs in a magnetic field (details are omitted here) is expressed in units of Hz as:

$$\Delta\nu_{Cs} = 9192631770 \text{ Hz}$$

This highly accurate piece of information can be rewritten using the definition of Hz = s^{-1} as:

$$\Delta\nu_{Cs} = 9192631770\ (1\ s)^{-1}$$

We then obtain the following definition:

$$1\ s = \frac{9192631770}{\Delta\nu_{Cs}}$$

This means that 1 s is 9192631770 times longer than the time of the $\Delta\nu_{Cs}$ transition, which is the new definition of 1 s.

In a similar manner, 1 m of distance is defined by using the velocity of light, c = 299792458 m s^{-1}. In other words, 1 m is defined as the distance that light travels in 1 s divided by 299792458. The definition of 1 s can be substituted into this definition of 1 m to afford:

$$1\ m = \frac{9192631770}{299792458}\frac{c}{\Delta\nu_{Cs}} = 30.633319\frac{c}{\Delta\nu_{Cs}},$$

which is the new definition of 1 m.

2-2. **Write** a new definition for 1 kg of mass using these new definitions with eight significant digits.

On the other hand, mass can also be discussed in terms of energy. The mass of a particle at rest, m, is equivalent to the energy having a frequency of ν (*i.e.*, the rest energy):

$$h\nu = mc^2$$

In this definition, a photon can also be recognized to have mass.

2-3. **Calculate** the apparent mass of a photon, m [kg], emitted from a laser pointer with a wavelength of 635 nm.

Problem 2. Does water boil or evaporate?

When an ideal gas is isothermally expanded from pressure p [bar] to p' [bar] ($p > p'$), the entropy change ΔS of the gas is

$$\Delta S\ [\mathrm{J\ K^{-1}\ mol^{-1}}] = -R \ln\left(\frac{p'}{p}\right) \qquad (1).$$

The enthalpy change when liquid water evaporates to water vapor at p_0 [bar] is ΔH_v° [J mol^{-1}], and the entropy change is ΔS_v° [J K^{-1} mol^{-1}]. Let us suppose these values do not depend on temperature, and the gas is an ideal gas. In this case, when liquid water evaporates to water vapor at p_1[bar], the enthalpy change is ΔH_v [J mol^{-1}] = ΔH_v°, and the entropy change is ΔS_v [J K^{-1} mol^{-1}] = $\boxed{\text{(a)}}$.

1. **Write** the appropriate formula for blank (a).

For the following questions, assume that $\Delta H_v^\circ = 4.070 \times 10^4\ \mathrm{J\ mol^{-1}}$ and that, $\Delta S_v^\circ = 1.091 \times 10^2\ \mathrm{J\ K^{-1}\ mol^{-1}}$ at p_0 = 1 bar.

2. **Calculate** the boiling point of water at 1 bar.

3. **Calculate** the saturated vapor pressure of water at 87 °C.

4. **Calculate** the Gibbs energy change per mole when water evaporates at 87 °C at a humidity of 50%. The humidity represents the ratio of the actual partial pressure of water vapor relative to the saturated vapor pressure of water.

A container with a piston like that shown in Figure 1 is filled with 0.10 mol of Ar and 1.00 mol of water (liquid and vapor). The temperature of the entire container is 87 °C and the total pressure is 1 bar. It is assumed that the volume of the liquid or cup is negligible with respect to that of the gas, and that the temperature of water and Ar is always maintained at 87 °C. In this initial situation, the partial pressure of Ar is $\boxed{\text{(b)}}$ bar, the partial pressure of water vapor is $\boxed{\text{(c)}}$ bar, the volume of the gas is $\boxed{\text{(d)}}$ L, and the number of moles of liquid water is $\boxed{\text{(e)}}$ mol.

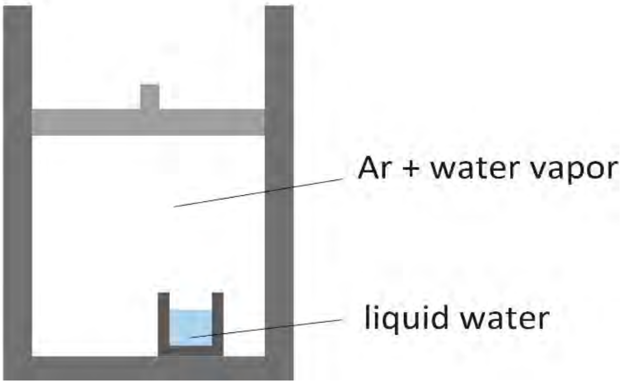


Figure 1. A container with a piston containing Ar gas, water vapor and liquid water in a cup.

The piston is then pulled back quickly to fix the gas volume to 15.8 L. At the moment when the piston is pulled, the partial pressure of Ar decreases to $\boxed{\text{(f)}}$ bar and the partial pressure of water vapor decreases to $\boxed{\text{(g)}}$ bar. In this situation, the water will boil, because the total pressure of the gas is lower than the saturated vapor pressure of water at 87 °C. The partial pressure of water vapor increases due to the boiling until the boiling eventually stops. When the boiling stops, the number of moles of liquid water is $\boxed{\text{(h)}}$ mol. After that, evaporation proceeds until equilibrium is reached. At equilibrium, the number of moles of liquid water is $\boxed{\text{(i)}}$ mol.

5. **Calculate** the appropriate numerical values for blanks (b) - (i).

Problem 3. Molecules meet water and metals

I. Dissolution of gases in water

For gases that are slightly soluble in water, there is a proportional relationship between the partial pressure, P, and the mole fraction, x, of the gas molecules dissolved in water (Henry's law):

$$P = k_{\mathrm{H}}x$$

Here, k_{H} is the Henry coefficient. The Henry coefficients of nitrogen, oxygen, and argon at 25 °C for water are 8.57×10^4, 4.42×10^4, and 4.02×10^4 bar, respectively. In the following questions, the compression of the water by the pressurized gas can be ignored.

Part 1. Decompression sickness

When a diver spends prolonged time at high depths, the high water pressure causes nitrogen molecules in the body to dissolve in the blood. If the diver rises too quickly to the surface, this dissolved nitrogen will form bubbles that damage the blood vessels and tissues. With the decompression sickness phenomenon in mind, answer the following questions regarding the dissolution of gas in water in a closed container.

1-1. **Calculate** the pressure [bar] underwater at a depth of 20.0 m. Here, the density of water is 1.00 g $\mathrm{cm^{-3}}$, the specific gravity of seawater is 1.02, the gravity acting on a mass of 1 kg is 9.81 N, and the atmospheric pressure is 1.01 bar.

1-2. At a temperature of 25 °C, 5.00 L of water, which is approximately equivalent to the blood volume of an adult, is added to a container with a piston, and the container is filled with nitrogen. Then, the pressure of the nitrogen is adjusted to the value calculated in Q1-1 by pushing down the piston, and sufficient time is allowed to pass for the gas–liquid equilibrium to be established. **Calculate** the amount of nitrogen [mol] dissolved in water.

1-3. The piston is then moved to lower the pressure to 0.800 bar, which is approximately equal to the partial pressure of nitrogen in the atmosphere, and sufficient time is allowed for the vapor–liquid equilibrium to be established. **Calculate** the volume [L] of nitrogen at 25 °C that is released into the gas phase from the nitrogen dissolved in water in Q1-2.

Part 2. Sparkling beverages

The dissolution of high-pressure gas in water in a closed container is also relevant to sparkling beverages.

2-1. A container (V = 570 mL) is filled with water (V_l = 500 mL) and pressurized with CO_2 gas (P_0 = 50 atm), before it is allowed to stand at 10 °C until the vapor–liquid equilibrium is established. **Calculate** the pressure of CO_2 [atm] in the container and the amount of CO_2 [mol] dissolved in the water. The Henry coefficient of CO_2 for water at 10 °C is $k_{\mathrm{H}} = 0.104 \times 10^4$ atm, and we will consider that the reaction of CO_2 in water can be ignored.

2-2. Carbon dioxide (N L) dissolved in water (1 L) is called N GV (Gas Volume), where N is the volume of this gas at 0 °C and 1 atm. **Calculate** how many GV the aqueous solution obtained in Q2-1 corresponds to.

2-3. When this container is heated to 50 °C, **calculate** the pressure of the gas [atm] in the container and the amount of CO_2 [mol] dissolved in water. Here, the Henry constant of CO_2 at 50 °C is 0.283×10^4 atm.

Part 3. Removal of dissolved oxygen

3-1. A container (2.0 L) filled with water (1.0 L) has been left exposed to air for a long time at 1.0 bar and 25 °C. **Calculate** the mole fraction and mass of oxygen [mg] dissolved in the water. Here, assume that the atmosphere contains 21% oxygen.

3-2. The atmosphere in contact with this water is replaced with 1.0 bar argon and sealed, and the mixture is stirred sufficiently for the gas–liquid equilibrium to be established at 25 °C. **Calculate** the mole fraction of oxygen dissolved in the water. Here, the evaporation of water can be ignored during the gas replacement.

3-3. **Calculate** how many times the above operation must be repeated to reduce the mole fraction of dissolved oxygen to 1 ppt (= 10^{-12}) or less.

Part 4. Complex formation in water

Consider a mixture of two different gases (A and B) for which Henry's law holds. When gas molecules A and B do not interact with each other in either the gas phase or in water, the amount of each that will be dissolved in water is determined only by its partial pressure and does not depend on the partial pressure of the other gas. However, let us now consider the case in which A and B form a complex AB when they are dissolved in water:

$$\mathrm{A}\,(l) + \mathrm{B}\,(l) = \mathrm{AB}\,(l)$$

Let x_i (i = A, B, AB) be the mole fraction of the dissolved species, and let K_{AB} be the equilibrium constant for the above equation:

$$K_{\mathrm{AB}} = x_{\mathrm{AB}}/x_{\mathrm{A}}x_{\mathrm{B}}.$$

Suppose that water (V_l=1.00 L) and a gas mixture are filled into a container (V = 2.00 L) at 25° C. The Henry coefficients of A and B are 1.0×10^4, and 2.0×10^4 bar, respectively, and K_{AB}= 500. Answer the following questions:

4-1. The initial partial pressures of each gas, P_{A}^{0} and P_{B}^{0}, are both 2 bar. **Calculate** the pressure of each gas and the mole fractions of the dissolved gas molecules after the equilibrium is established.

4-2. **Calculate** the percentage of the mole fraction of dissolved gas B relative to that found in Q4-1 when the initial partial pressure of gas A is increased to 10 bar.

II. Adsorption of molecules on a metal surface

Let us consider the adsorption of gas molecules on a metal surface under the following assumptions: (1) There are specific sites on the metal surface where the gas molecules are adsorbed; (2) when a gas molecule occupies an adsorption site, the site is blocked so that other molecules cannot be adsorbed at the occupied site; (3) the probability of the adsorption of a molecule onto an empty site does not depend on whether or not a molecule is adsorbed at the neighboring sites; *i.e.*, molecules adsorbed on the metal surface do not interact with each other. Here, we define parameters relevant to the adsorption: S_0 [mol m^{-2}] is the density of adsorption sites; $\theta = a/S_0$ is the coverage, where a [mol m^{-2}] is the number of adsorbed molecules per unit surface area; S [mol m^{-2}] is the number of empty sites per unit area. Answer the following questions:

Part 5. Adsorption isotherm

5-1. The surface is exposed to a gas at a pressure P. Let the reaction rate constants of adsorption and desorption be k_a and k_d, respectively. **Write** an expression for the rates of adsorption and desorption in terms of $P, k_a, k_d, a, and\ S$.

5-2.Adsorption–desorption equilibrium is achieved when the adsorption and desorption rates are equal.

Let the equilibrium constant be $K = k_a/k_d$. **Write** an expression for the coverage θ at equilibrium in terms of K and P.

5-3. **Express** P in terms of θ and K for the case of extremely low coverage ($\theta \ll 1$).

5-4. Metal particles (m = 100 g) are placed in a container (V = 1.00 m^3) and a gas A is introduced into the container at an initial pressure of P_0 = 100 Pa. The gas pressure decreases and then reaches a constant value. **Calculate** the pressure of the gas [Pa] in the container and the amount of gas molecules [mol] adsorbed on the surface of the metal particles. Here, assume that the surface area of the metal particles per unit mass is A = 10.0 m^2 g^{-1}; S_0 = 1.66 × 10^{-5} mol m^{-2}; K = 10.0 Pa^{-1}; the temperature of the system is constant at T = 300 K and the volume of the metal particles is negligible.

Part 6. Adsorption of mixed gas

6-1. Consider the case in which two gases (A and B) are adsorbed on the metal surface. Assume that these gases do not interact or react with each other (neither in the gas phase nor on the surface after adsorption), and that an adsorption site can be occupied by either A or B. **Express** the coverage of A and B (θ_{A} and θ_{B}) in terms of the partial pressures of the gases (P_{A} and P_{B}) as well as the adsorption and desorption equilibrium constants (K_{A} and K_{B}).

6-2. When gases A and B are filled into the same container as in Q5-4, the partial pressures of each gas after reaching equilibrium are measured to be P_{A} = 70.0 Pa and P_{B} = 30.0 Pa. **Calculate** the coverage of each gas adsorbed on the surface of the metal particles. Let the adsorption and desorption equilibrium constants of gases A and B be K_{A} = 10.0 Pa^{-1} and K_{B} = 20.0 Pa^{-1}, respectively.

6-3. Under the conditions where $K_{\mathrm{A}}P_{\mathrm{A}} \ll 1$ and $K_{\mathrm{B}}P_{\mathrm{B}} \ll 1$, how can the coverage θ_{A} and θ_{B} be approximated? **Write** approximate expressions in terms of $P_{\mathrm{A}}, P_{\mathrm{B}}, K_{\mathrm{A}},$ and K_{B}.

6-4. Gases A and B are introduced into the container described in Q5-4 and the system reaches adsorption–desorption equilibrium. The partial pressure of gas A is found to be 70.0 Pa, which is the same as in Q6-2, whereas the partial pressure of gas B is 60.0 Pa, which is twice that in Q6-2. **Calculate** the percentage of coverage of gas A compared to that under the conditions of Q6-2.

III. Note

Comparing Part 4 and 6, we understand the following difference between gas dissolution in liquid and adsorption on metal surface. Under conditions where Henry's law holds, the dissolution of molecules into a liquid depends only on the partial pressure of the gas of interest. The same applies to adsorption onto a metal surface when the coverage is sufficiently low. However, even under conditions where Henry's law holds, if there is interaction and association between the molecules of the different species in the liquid, the amount of each species dissolved will depend not only on the partial pressure of the gas, but also on the partial pressure of the molecules of the other species. In contrast, as the coverage increases in the case of adsorption, the amount of adsorption for a given species will depend on the partial pressure of the molecules of the other species even if there is no interaction between the molecules of the different species. This is due to the finite number of sites where the molecules can be adsorbed on the metal surface.

Problem 4. Synthesis of diamonds

Diamond, one of the allotropes of carbon, is used not only for jewelry, but also in various tools that take advantage of its extremely high hardness. Natural diamond is considered to be produced under high-pressure and high-temperature conditions in the bowels of the earth. Currently, several techniques to synthetically generate diamonds are available, and massive amounts of artificial diamonds are used industrially.

Let us examine the stability of diamonds at ambient pressure and temperature. The enthalpies of combustion ($\Delta_c H°$) for 1 mole of graphite, diamond, and C_{60}, as well as the standard entropy changes ($\Delta S°$) for the conversion of 1 mole of graphite to diamond or C_{60} under ambient conditions (1 bar, 298.15 K) are summarized in Table 1. For graphite and diamond, 1 mole represents 12.01 g.

Table 1. Thermodynamic data for carbon allotropes

	$\Delta_c H°$ / kJ mol^{-1}	$\Delta S°$/ J K^{-1} mol^{-1}
Graphite	−393.5	(0)
Diamond	−395.3	−3.25
C_{60}	−25965	1.54

1. **Calculate** the change in enthalpy, entropy, and Gibbs free energy for the transformation of 1 mole of graphite into diamond and into C_{60} under ambient conditions. Then, **rank** graphite, diamond, and C_{60} in order of decreasing stability in terms of Gibbs free energy.

2. Under ambient conditions, diamond does not transform into graphite, which is energetically more stable than diamond. **Explain** why this transformation does not occur.

The enthalpies of combustion for graphite and diamond are comparable, and therefore, it is difficult to determine the change in enthalpy from graphite to diamond precisely via the calculation method used in Q1. To overcome this difficulty, the temperature dependence of the electromotive force of the following battery was measured:

$$\text{Pt, C(graphite)} + CaC_2 + CaF_2 \,||\, CaF_2 \,||\, CaF_2 + CaC_2 + \text{C(diamond), Pt} \qquad (1)$$

This is a solid-state battery in which diamond is used as the cathode (positive electrode) and graphite is used as the anode (negative electrode). On the cathode, the diamond is reduced and CaC_2 is produced. On the anode, CaC_2 is oxidized and graphite is produced.

3. **Write** the half-reactions occurring on the cathode and the anode.

4. The electromotive force of this battery over the temperature range 940–1260 K can be expressed as a function of the absolute temperature T according to:

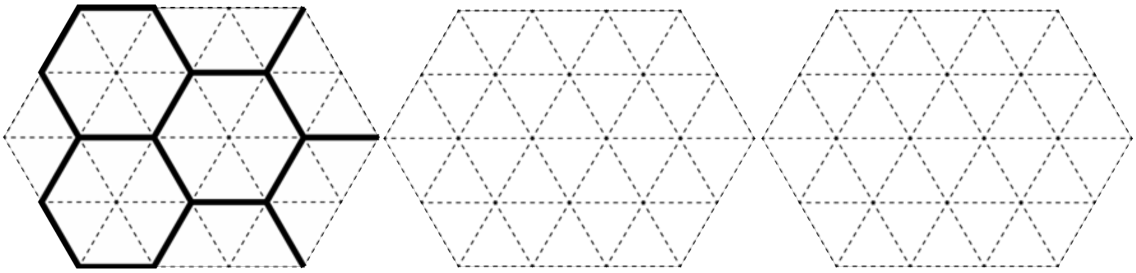
$$E = 11.4 + 0.0481T \text{ [mV]} \qquad (2)$$

Calculate the change in enthalpy and entropy for the conversion of 1 mole of graphite to diamond in this temperature range.

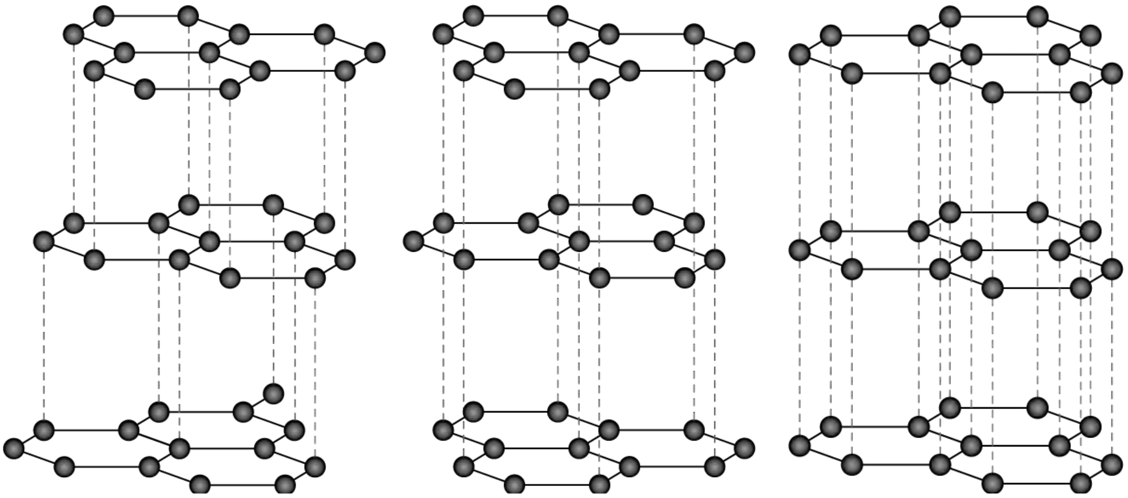
One of the techniques to synthesize diamond is the direct conversion of graphite into diamond by applying high pressure to graphite. The mechanism underlying this conversion is known as the puckering mechanism.

Graphite is composed of stacked layers of graphene. For each layer, there are three possible relative positionings in which the graphene layer can be placed. From here on, these geometries are referred to as A, B, and C. The crystal structures of graphite can exhibit one of three stacking patterns: AAAAAA… (1H where H stands for hexagonal), ABABAB… (2H), and ABCABC… (3R where R stands for rhombohedral). The most stable structure is 2H, and typical graphite also contains a small amount of the 3R structure.

5. One of the geometries of graphene is shown below (left, set as A). **Draw** the other two geometries (B and C, you do not have to distinguish these two).

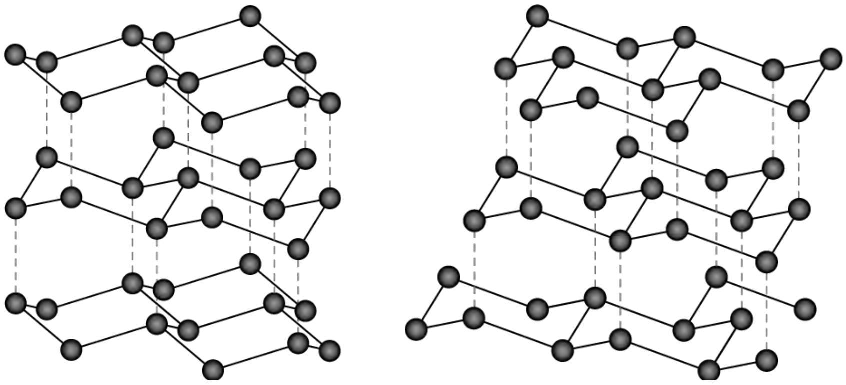


6. **Assign** the following three crystal structures as the 1H, 2H, and 3R structures.

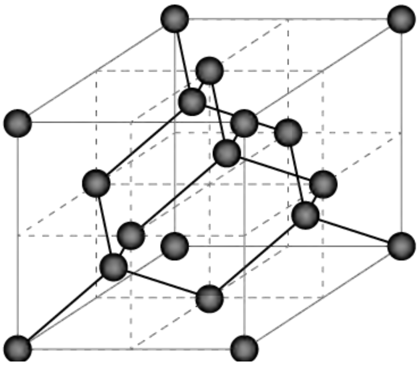


Diamond (cubic crystal) is generated from the 3R structure by displacing each carbon atom in a direction perpendicular to the plane. A crystal structure similar to that of diamond is obtained by displacing each carbon atom of the 1H structure in a direction perpendicular to the plane. The crystal structure generated from the 1H structure is called lonsdaleite, and is a hexagonal crystal. It has been theoretically predicted that pure lonsdaleite would be harder than diamond.

7. **Assign** the following crystal structures as diamond and lonsdaleite.



8. Under ambient conditions, the distance between covalently bonded carbon atoms in graphite is 1.42 Å, while the distance between the graphene layers of graphite is 3.35 Å; the distance between covalently bonded carbon atoms in diamond is 1.54 Å. **Calculate** the density of graphite and diamond under ambient conditions. The unit cell of diamond is shown below:



In the puckering mechanism, there are two energy barriers: The barrier for the transformation from the 2H structure to the 3R structure (Step 1), and the barrier for the transformation of the carbon atoms from a planar to a tetrahedral configuration via puckering (Step 2).

9. The activation energy in Step 2 will be small if there is no volume change between graphite and diamond. **Calculate** the distance between the graphene layers of graphite for which there would be no volume change. Assume that the distances between the covalently bonded carbon atoms in graphite and diamond do not change on account of the applied pressure.

[Note] The direct conversion method described above requires high temperature (3000–4000 K) to increase the reaction rate in addition to high pressure (~ 10 GPa). A new conversion method, in which the graphite is first melted with metals to break the covalent bonds among the carbon atoms before new covalent bonds are generated under high-pressure conditions where diamond is thermodynamically stable, has been developed.

In addition to the direct conversion method, diamond can also be synthesized by a chemical vapor deposition (CVD) method. In this technique, a thin layer of diamond is grown on a substrate exposed to a gas containing hydrocarbon radicals prepared by heating or electrical discharge.
As an example, let us consider a diamond synthesis using methane and hydrogen molecules as sources. The reaction rates for the synthesis of diamond and graphite on the substrate, v_d and v_g, can be expressed in terms of the concentration of active hydrocarbons (such as CH_3 radicals) near the surface

of the substrate, C_C, and the rate constants, k_d and k_g, according to:

$$v_d = k_d C_\mathrm{C} \tag{3}$$

$$v_g = k_g C_\mathrm{C} \tag{4}$$

At the same time, diamond and graphite on the substrate are removed in the form of gaseous species (typically hydrocarbon radicals) due to reaction with hydrogen atoms near the surface. This process is called etching. The reaction rates for the etching of diamond and graphite from the substrate, v'_d and v'_g, are expressed in terms of the concentration of hydrogen atoms near the surface of the substrate, C_H, and the rate constants, k'_d and k'_g, according to:

$$v'_d = k'_d C_\mathrm{H} \tag{5}$$

$$v'_g = k'_g C_\mathrm{H} \tag{6}$$

10. **Write** an expression for the concentration of hydrogen atoms near the surface of the substrate in terms of C_C and the appropriate rate constants when the amount of graphite on the substrate remains constant.

11. **Write** an expression for the net growth rate of diamond on the substrate in terms of v_d and the appropriate rate constants under the condition where the amount of graphite on the substrate remains constant. (Based on this result, the condition that the reaction constants must satisfy can be obtained.)

To determine the activation energy of this process experimentally, the growth rate of diamond on the substrate is used. The measured growth rates of the thicknesses of the diamond layer on the diamond substrate for different substrate temperatures and gas compositions are shown in Table 2. In the case where only hydrogen gas was used, the substrate became thinner due to etching (eq. 5).

Table 2. Growth rates of diamond prepared by the chemical vapor deposition method

Substrate temperature	900 °C	1100 °C
CH_4 13% + H_2 87%	30.34 μm h^{-1}	63.43 μm h^{-1}
H_2 100%	−1.58 μm h^{-1}	−5.52 μm h^{-1}

Although the elementary steps of the synthesis and etching of diamond are not known, it is reasonable to define the activation energy for the total reaction, because the reaction rates for the synthesis and etching on the substrate follow the Arrhenius equation.

12. **Calculate** the activation energy of the synthesis of diamond when the composition of the source gas is CH_4 (13%) + H_2 (87%). Assume that the effect of etching by hydrogen gas is negligible compared to the synthesis of diamond.

13. **Calculate** the pre-exponential factor of the Arrhenius equation and the activation energy for the etching of diamond by hydrogen atoms.

14. When the experiment is conducted using a CH_4 (1%) + H_2 (99%) source gas mixture at 1000 °C, the thickness of the substrate does not change. Assuming that the etching of diamond by hydrogen atoms and the synthesis of diamond occur independently, *i.e.*, that the pre-exponential factor of the etching and the activation energies of the etching and diamond synthesis are the same as the values obtained in the previous questions, **calculate** the temperature of the substrate where the growth rate of diamond is 0.50 μm h^{-1} using the CH_4 (1%) + H_2 (99%) source gas. By controlling the reaction rate of the synthesis of diamond and etching appropriately as shown in this problem, a very thin diamond coating can be achieved.

Problem 5. Count the number of states

Boltzmann defined entropy as a measure of the number of possible microscopic states of a system, W, as:

$$S = k_\mathrm{B} \ln W$$

Here, k_B is the Boltzmann constant. Hereafter, it is assumed that neither energy nor particles are exchanged between the system of interest and the surrounding environment, and that the system is in equilibrium at a constant temperature. In addition, the gas atoms and molecules (henceforth referred to as 'molecules') are assumed to behave as an ideal gas.
Now, let us explore the entropy of gas molecules using this definition in Questions 1–7.

Assume that ten molecules are arranged in two chambers separated by a wall, A and B, with four molecules in A and six in B. We describe this microscopic state as (4,6).

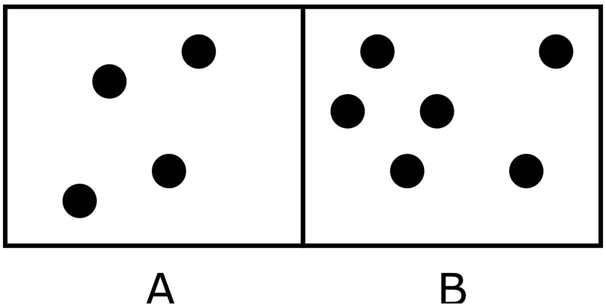


Figure 1. Example of a microscopic state in which ten molecules are distributed in two chambers.

The number of cases in which 10 indistinguishable molecules result in a (4,6) arrangement is calculated as:

$$W(4,6) = {}_{10}C_4 = 10!/6!\,4! = 210$$

For (5,5):

$$W(5,5) = {}_{10}C_5 = 10!/5!\,5! = 252$$

Thus, $W(5,5)$ is larger than $W(4,6)$. In this system, the number of cases represents the number of states for a specific arrangement of gas molecules in the two chambers.

1. **Calculate** $W(40,60)$ and $W(50,50)$ with 2 significant digits using the following approximate formula for a factorial:
   $$n! \simeq \sqrt{2\pi n}\left(\frac{n}{e}\right)^n$$

Removing the boundary wall that separates the two chambers in Figure 1 allows the molecules to move throughout the entire container. Assume that it is possible to measure the arrangement of the molecules instantly after the removal of the wall. If this measurement is performed a sufficiently high number of times, the probability that a state with an arrangement (n,m) will be found can be calculated.

2. **Calculate** the arrangement $(n^*, N - n^*)$ with the highest probability of occurrence for $N = 10$ and 100, as well as the corresponding probability of occurrence for each state. Moreover, **calculate** the probability of observing a state in which n^* is in the range $n^* - 0.02\,N \leq n^* \leq n^* + 0.02\,N$ for $N = 10$ and $N = 100$. Here both N and n^* are integers.

Let us consider the space inside chamber A, whose volume V_1 is composed of small subsections ΔV. As a molecule in the chamber is located in one subsection at any given time, the total number of possible locations of the molecule in the chamber W_A is given by $W_\mathrm{A} = V_1/\Delta V$. Likewise, the number of possible locations for a molecule that can access the whole chamber, whose volume is V_2, can be written as $W_{\mathrm{AB}} = V_2/\Delta V$. Thus:

$$\frac{W_{\mathrm{AB}}}{W_{\mathrm{A}}} = \frac{V_2/\Delta V}{V_1/\Delta V} = \frac{V_2}{V_1}$$

Now suppose that chamber A is filled with n moles of gas molecules, while no molecules are present in chamber B (State 1), *i.e.*, chamber B is a vacuum. Then, the boundary wall is removed so that the gas in chamber A expands spontaneously throughout the entire container (State 2) at a constant temperature.

3. **Express** the change in entropy $\Delta S = S_2 - S_1$ in terms of the gas constants R, V_1, and V_2.

4. **Calculate** the difference in entropy for an isothermal expansion of the two-chamber system described above when chamber A is initially filled with oxygen molecules (0.30 mol). Use $V_1 = 0.10$ m^3 and $V_2 = 0.40$ m^3.

As shown in Figure 2, let State 1 be the case in which chambers A and B, whose volumes are identical, are each filled with a different kind of gas molecules. Suppose that these gases are mixed isothermally in a chamber with the same volume as chambers A and B (State 2).

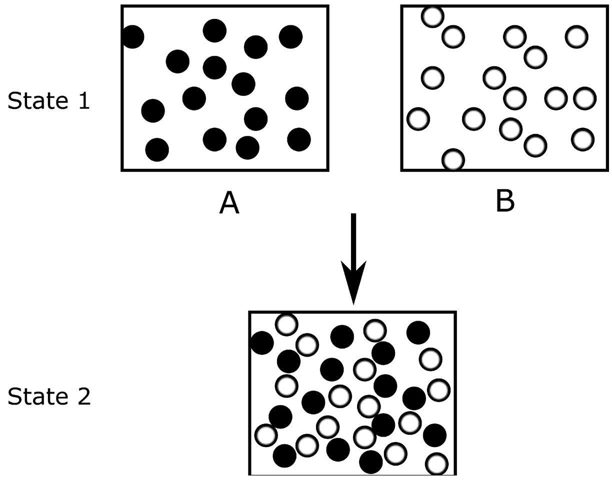


Figure 2. Isothermal mixing of different kinds of gas molecules in chambers with the same volumes.

5. **Calculate** the difference in entropy associated with the mixing process.

As shown in Figure 3, two kinds of gas molecules, α (n_α moles) and β (n_β moles), are separately filled into chambers A (volume V_{A}) and B (volume V_{B}), respectively, at a temperature T and a pressure P (State 1). Let State 2 represent the complete mixture of the gas molecules after removing the boundary wall.

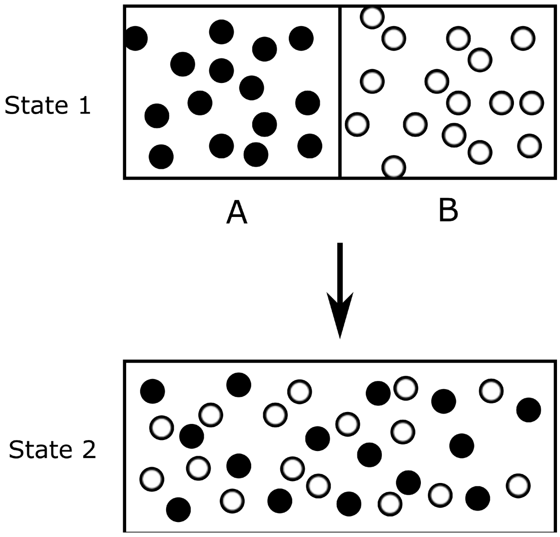


Figure 3. Mixing of different kinds of gas molecules accompanied by expansion.

6. **Express** the entropy change $\Delta S = S_2 - S_1$ from State 1 to State 2 in terms of R, n_α, and n_β.

7. Instead of being filled with molecules of gas β as in Q6, assume that chamber B is filled with molecules of gas α (n_β moles) (State 1), before the boundary wall is removed (State 2). **Calculate** the entropy difference from State 1 to State 2.

In Questions 8 and 9, we will explore the entropy associated with the orientation of molecules in a crystal.

According to the third law of thermodynamics, the entropy of a pure and perfect crystal approaches zero as the absolute temperature approaches 0 K. However, in a real molecular crystal, the molecules in the crystal may not be completely aligned at low temperatures. Thus, even when the absolute temperature approaches 0 K, the crystal can retain a finite nonzero entropy value. This is called residual entropy. For example, because carbon monoxide (CO) is a heterogeneous diatomic molecule, CO molecules have a definite orientation in the CO crystal. Figure 4A shows that the orientation of some molecules is disordered. Because a CO molecule can exhibit two different orientations in the crystal, the residual entropy per mole if the molecular orientations are completely random in the crystal would be:

$S = k_B \ln 2^{N_A} = R \ln 2 = 5.7\ \mathrm{J\ K^{-1}\ mol^{-1}}$

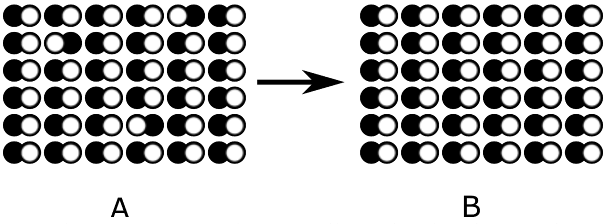


Figure 4. Schematic representation of disorder in the molecular orientation in a CO crystal. A: Some CO molecules are oriented in the opposite direction. B: An ideal crystal without any disorder in the molecular orientation.

8. Every methane (CH_4) molecule in a crystal is surrounded by four methane molecules in a tetragonal fashion. **Calculate** the molar residual entropy of isotopically labeled methane, H_3CD, when the molecules are completely randomly oriented.

Figure 5 shows a molecular arrangement of ice (solid H_2O); a central water molecule is coordinated by four water molecules in a tetragonal fashion.

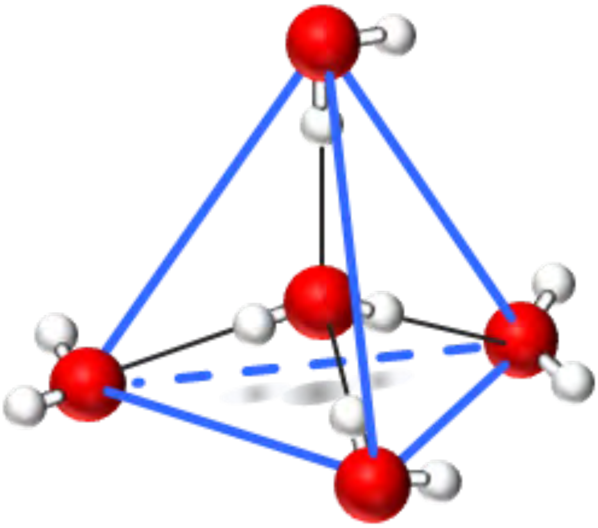


Figure 5. Arrangement of water molecules in an ice crystal.

All the water molecules are arranged in the crystal according to the so-called 'ice rules':

(1) Each hydrogen atom must be located between two adjacent oxygen atoms.

(2) Two of the four hydrogen atoms that surround each oxygen atom must be positioned closer to that oxygen than to the neighboring oxygen atoms, while the other two hydrogens should be located closer to one of the neighboring oxygen atoms.

9. Now, let us estimate the molar residual entropy of ice using the following procedures.

9-1. There are two stable sites for a hydrogen atom between two adjacent oxygen atoms. **Calculate** the number of possible configurations of hydrogen atoms in a crystal composed of 1 mole of water (N_A molecules) without any constraints of the ice rules.

9-2. **Calculate** the number of possible configurations for four hydrogen atoms around the central oxygen atom in Figure 5.

9-3. Some of the configurations calculated in Q9-2 such as $(H_3O)^+$, in which three protons are arranged closest to one oxygen atom, violate the ice rules. **List** all chemical species that break the ice rules and **calculate** the number of configurations for each species. Then, **calculate** the number of configurations that satisfy the ice rules.

9-4. Based on these considerations, **calculate** the molar residual entropy when the orientation of water molecules is completely random in ice.

Problem 6. The path of chemical reactions

The structure of a molecule and its changes can be understood in terms of the potential energy. Consider the motion of the two atoms that make up a diatomic molecule AB. The velocity of the atoms A and B, whose masses are m_A and m_B, are denoted as v_A and v_B. The kinetic energy of the system is given by

$$T = \frac{1}{2} m_\mathrm{A} v_\mathrm{A}^2 + \frac{1}{2} m_\mathrm{B} v_\mathrm{B}^2 \tag{1}$$

Each atom, A and B, has three degrees of freedom, and there are six degrees of freedom in total. Because the motion of the molecule AB consists of the part of the translation and rotation of the whole molecule and that of the relative motion of the two atoms, the above equation can be rewritten as

$$T = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} \mu (v_\mathrm{A} - v_\mathrm{B})^2 \tag{2}$$

where μ is the effective mass defined as

$$\mu = \left(\frac{1}{m_\mathrm{A}} + \frac{1}{m_\mathrm{B}} \right)^{-1} \tag{3}$$

1. **Calculate** M_1 and v_1 in Equation (2). M_1 and v_1 are quantities with dimensions of mass and velocity, respectively.

The geometry of a diatomic molecule is determined only by the relative position (coordinates) of the two atoms, *i.e.*, the distance between them, *R*, which corresponds to the vibrational motion of the molecule. The potential energy *E* as a function of *R* near the equilibrium structure can be approximated by

$$E(R) - E_0 = \frac{1}{2} k (R - R_0)^2 \tag{4}$$

where E_0 is the reference energy and R_0 is the equilibrium internuclear distance. Under normal conditions, the molecule adopts a stable structure with the lowest energy. In this equation, *k* is a physical quantity corresponding to the spring constant that increases with increasingly stronger bonds. This quadratic representation is called the harmonic oscillator approximation, and *k* is linked to the frequency ν via the effective mass.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{5}$$

2. Suppose that diatomic molecule XY forms either single or double bonds. What relationship can be expected for each *k* (k^S and k^D) and their corresponding equilibrium internuclear distances ($R^\mathrm{S}{}_0$ and $R^\mathrm{D}{}_0$)? **Choose** only one answer.

☐ $k^\mathrm{S} > k^\mathrm{D}$ and $R^\mathrm{S}_0 > R^\mathrm{D}_0$	☐ $k^\mathrm{S} > k^\mathrm{D}$ and $R^\mathrm{S}_0 = R^\mathrm{D}_0$	☐ $k^\mathrm{S} > k^\mathrm{D}$ and $R^\mathrm{S}_0 < R^\mathrm{D}_0$
☐ $k^\mathrm{S} = k^\mathrm{D}$ and $R^\mathrm{S}_0 > R^\mathrm{D}_0$	☐ $k^\mathrm{S} = k^\mathrm{D}$ and $R^\mathrm{S}_0 = R^\mathrm{D}_0$	☐ $k^\mathrm{S} = k^\mathrm{D}$ and $R^\mathrm{S}_0 < R^\mathrm{D}_0$
☐ $k^\mathrm{S} < k^\mathrm{D}$ and $R^\mathrm{S}_0 > R^\mathrm{D}_0$	☐ $k^\mathrm{S} < k^\mathrm{D}$ and $R^\mathrm{S}_0 = R^\mathrm{D}_0$	☐ $k^\mathrm{S} < k^\mathrm{D}$ and $R^\mathrm{S}_0 < R^\mathrm{D}_0$

For diatomic molecules in reality, bonds break when R becomes sufficiently large; then atoms no longer interact with each other and the energy remains unchanged. The following equation, the so-called Morse potential approximation, is often used instead of the quadratic equation described above to better describe the potential energy of a molecule.

$$E(R) - E_0 = D_e\{1 - e^{-a(R-R_0)}\}^2 \qquad (6)$$

where D_e, a, and R_0 are constants.

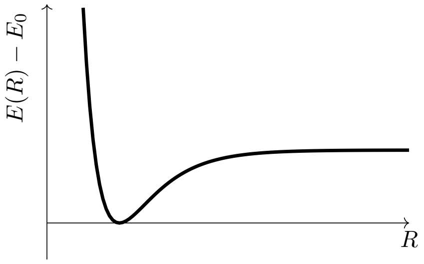
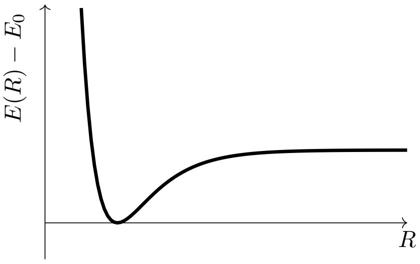


Figure 1. Morse potetinal

3. **Draw** D_e and R_0 in the figure below.



4. **Choose** all correct explanations for the harmonic and Morse potential approximation energy curves.

☐ For the harmonic oscillator approximation (Eq. 4) and the Morse potential approximation (Eq. 6), the equilibrium internuclear distance is the same.
☐ In the region where R is long, the Morse potential approximation is lower in energy than the harmonic oscillator approximation.
☐ In the region where R is short, the Morse potential approximation and the harmonic oscillator approximation coincide.
☐ As a increases in the Morse potential approximation, the width of the well becomes narrower.

For diatomic molecules, the energy E is represented as a one-dimensional curve that depends only on R (Figure 1), while for general polyatomic molecules, it is a multi-dimensional surface, *i.e.*, a point on such an energy surface corresponds to the structure of the molecule. The figure shows a bird's-eye view of the energy surface, wherein the direction of the x-axis is the Morse oscillator and the direction of y-axis is the harmonic oscillator.

$$E(x,y) = 5.0\{1 - e^{-2.0(x-1.0)}\}^2 + 20.0(y-2.0)^2$$

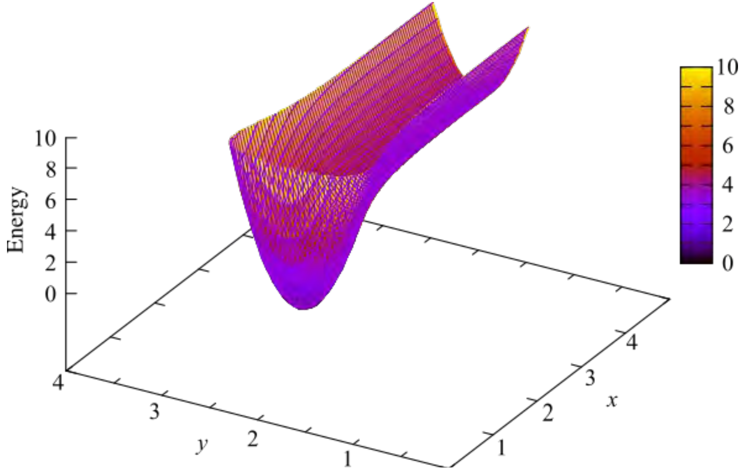
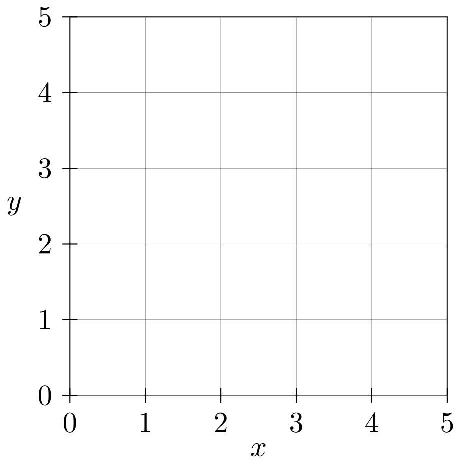


Figure 2. Energy surface in two dimensions

5. **Sketch** the contour map of this energy surface with the *x* axis as the horizontal axis and the *y* axis as the vertical axis.



The molecular geometry of a triatomic molecule can be determined by specifying three parameters that characterize the structure, such as both internuclear distances and the bond angle. A contour map of the potential energy surface of a typical triatomic molecular reaction A+BC → AB+C is shown in Figure 3.

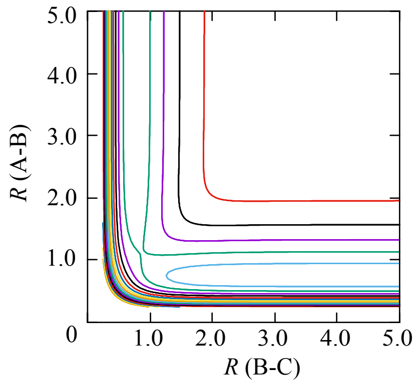
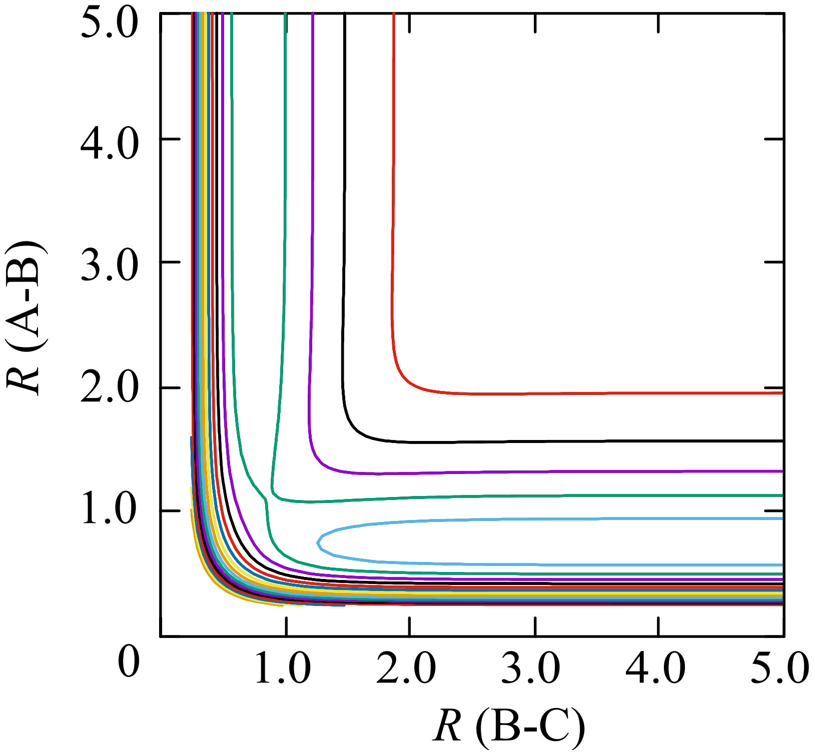


Figure 3. Contour map of the reaction A+BC → AB+C

Here, A collides with a diatomic molecule BC, producing a new diatomic molecule AB and monatomic C. Assuming that the three atoms are always on the same line, two degrees of freedom allow us to completely determine the arrangement of the three atoms in the reaction process. In Figure 3, the vertical axis represents the internuclear distance of AB while the horizontal axis represents the internuclear distance of BC.

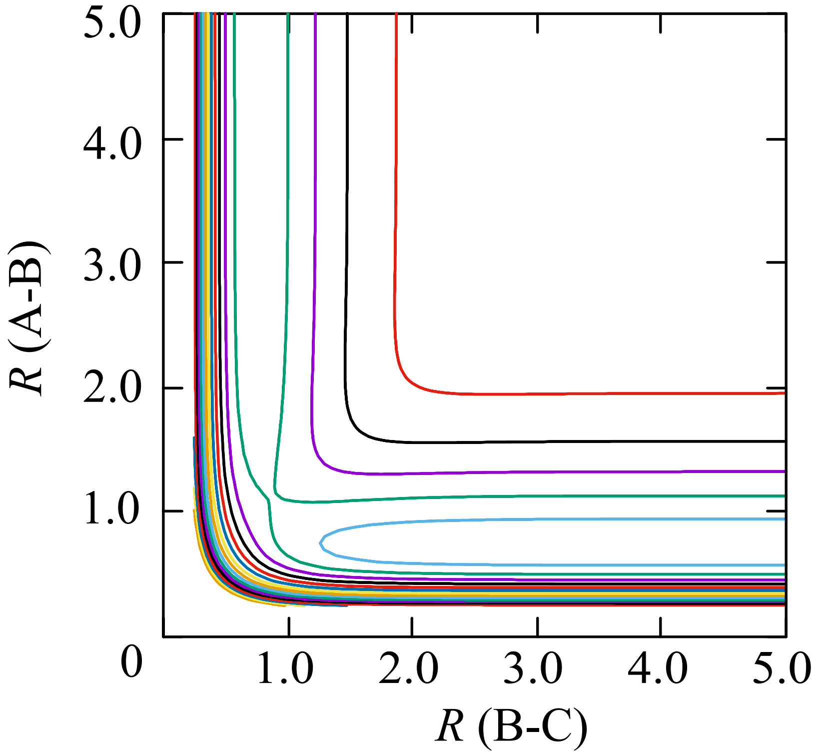
Thus, the structural change in the reaction can be interpreted as a pathway on the potential energy plane. Fukui has defined this pathway as the intrinsic reaction coordinate (IRC).

6. As a reaction path, consider a path that always minimizes the potential energy in any direction other than the reaction path. **Sketch** this path in the figure below.



In the actual reaction, the nuclei, which do not participate directly in the recombination of atoms, also oscillate and do not stop, which is the so-called 'bobsleigh effect'. This corresponds to a motion in the direction perpendicular to the reaction coordinates.

7. Suppose that BC is vibrating before A collides, and that AB is also vibrating after the collision. **Sketch** a path of this reaction in the figure below.



Let's generalize further to consider reactions in more complex molecules.

$$CH_3CH_2F \rightarrow CH_2{=}CH_2 + HF$$

As a result of this dissociation reaction, all the atoms change their position, bond length, and angles. Let’s focus on the distances shown in Figure 4.

R_{CC}: The distance between the carbon atoms
R_{HF}: The distance between H_α and fluorine (F)
R_{CH}: The average of the four hydrogen (H) -carbon distances
R_{CM}: The distance between the center of mass of HF and CH_2CH_2 moieties.

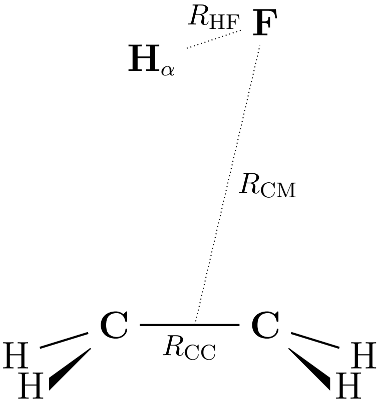


Figure 4. R_{CC}, R_{HF}, R_{CH}, and R_{CM} in the reaction $CH_3CH_2F \rightarrow CH_2{=}CH_2 + HF$

Figure 5 shows how the structure of the molecule changes while the reaction progresses. The vertical axis of the graph is the change in the interatomic distance ΔR from the beginning of the reaction, while the horizontal axis is the reaction coordinates, quantifying the progress of the reaction, which proceeds from left to right.

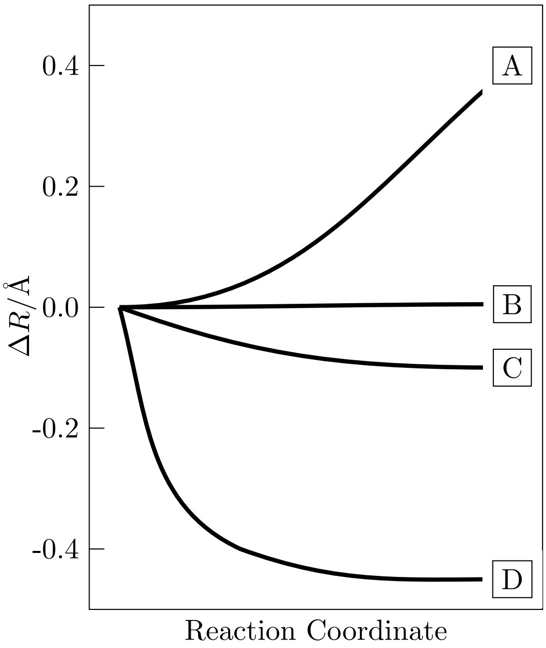


Figure 5. The change of R_{CC}, R_{HF}, R_{CH}, and R_{CM} during the reaction $CH_3CH_2F \rightarrow CH_2{=}CH_2 + HF$

8. **Match** A to D in the graph and the four distances mentioned above (R_{CC}, R_{HF}, R_{CH}, and R_{CM}).

Problem 7. Molecular vibrations and infrared spectroscopy

Consider the molecular vibration of hydrogen fluoride (HF). When HF diluted with a large excess of argon (Ar) is sprayed onto a cold cesium iodide (CsI) substrate at 12 K, the gas mixture condenses to generate a thin film on the substrate, which is known as the 'Ar matrix'. In this matrix, the rotation of HF can be ignored, and vibrational interactions between Ar and HF are also negligible. As a result, the molecular vibration of an isolated HF molecule can be measured independently using infrared (IR) spectroscopy, which quantitatively reveals molecular vibrations. Since CsI does not absorb IR irradiation, the spectrum of HF in the Ar matrix film can be readily measured using IR spectroscopy, and a strong IR absorption peak appears at 3953.8 cm^{-1} in the spectrum.

The frequency of the molecular vibration of HF, ν_{HF}, is given by:

$$\nu_{\mathrm{HF}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{\mathrm{HF}}}}\,.$$

Here, k denotes the spring constant of the chemical bond between H and F, which increases with increasing bond order. The reduced mass, μ_{HF}, is defined by:

$$\mu_{\mathrm{HF}} = \frac{m_{\mathrm{H}} m_{\mathrm{F}}}{m_{\mathrm{H}} + m_{\mathrm{F}}}\,,$$

where m_{H} and m_{F} are the atomic masses of H and F, respectively.

1. **Calculate** the wavenumber of the absorption peak of deuterium fluoride (DF) in an IR spectrum recorded using the Ar matrix technique. Let the spring constant of D–F be the same as that of H–F. The atomic masses of F, H, and D are 18.998, 1.0079, and 2.0141, respectively.

The quantized energy levels of molecular vibration, E_{v}, are defined by:

$$E_{\mathrm{v}} = \left(\mathrm{v} + \frac{1}{2}\right)h\nu \qquad (\mathrm{v} = 0,\ 1,\ 2,\ \cdots).$$

Here, v is the quantum number of vibration.
The molecular vibrational energy is distributed over the quantized energy levels, and the distribution ratio is proportional to the following factor:

$$\exp\left(-\frac{E_{\mathrm{v}}}{k_{\mathrm{B}}T}\right).$$

This factor is known as the Boltzmann factor. Here, k_{B} and T are the Boltzmann constant and absolute temperature, respectively. Although this factor is proportional to the distribution ratio, it is not equal to the probability for each level. Therefore, when all the Boltzmann factors are summed up, the sum is not unity, but instead yields q_{vib}, *i.e.*, the 'distribution function'. The actual distribution ratio at each level can be determined using the distribution function as the normalization constant.

2. **Write** the equation for the distribution function at a temperature, T, as the summation of a geometric series using the vibrational temperature, θ, which is defined as $\theta = h\nu/k_{\mathrm{B}}$.

3. **Calculate** the vibrational temperature of HF.

When the substrate temperature is raised to 26 K, the HF molecules begin to move in the Ar matrix, which yields a molecular associate of two HF molecules, (HF)$_2$, via hydrogen bonding as observed via a hydrogen-bonding-specific absorption peak in the IR spectrum. The hydrogen bond is generated from the overlapping wave functions of the electron of a lone pair and of a hydrogen atom. The molecule donating the hydrogen is called the ‘donor’, whereas the molecule receiving the hydrogen on the lone pair is called the ‘acceptor’. The hydrogen bond between two HF molecules is most stabilized when the lone pair of the acceptor and the H–F bond of the donor are aligned linearly. In this situation, the hydrogen atom is shared by the two fluorine atoms.

4. Based on this description, **draw** a chemical scheme for the molecular associate $(HF)_2$. Use a dotted line to represent the hydrogen bond, and show apparently the lone pairs of the accepter fluorine atom.

5. In the IR spectrum, a new absorption peak corresponding to the hydrogen-bonded acceptor is encountered. Does this new peak appear at a lower or higher wavenumber relative to the IR peak of the isolated HF molecule? **Choose** the correct shift with the most appropriate reason. Consider the fact that the H–F vibration becomes an F–H–F vibration with a different apparent mass, and that the bond order of the H–F bond is reduced when the hydrogen atom is shared by the two fluorine atoms.

   (1) k becomes smaller and μ becomes smaller; a prediction of the peak shift is difficult.
   (2) k becomes smaller and μ becomes larger, which results in a shift to a lower wavenumber.
   (3) k becomes larger and μ becomes smaller, which results in a shift to a higher wavenumber.
   (4) k becomes larger and μ becomes larger; a prediction of the peak shift is difficult.

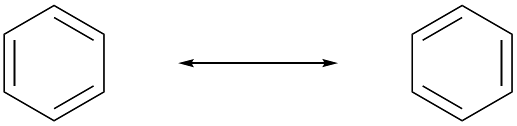
Active IR absorption modes are those with a vibrational energy transition of $\Delta v = +1$; such transitions are observed between various energy levels. At low temperature, however, only the $v = 1 \leftarrow v = 0$ transition needs to be considered. Here, the leftward arrow indicates an upward energy transition. This approximation is allowed because the occupation number at $v = 1$, g_1, is much lower than that at $v = 0$, g_0. As a result, higher energy transitions such as $v = 2 \leftarrow v = 1$ can be ignored.

6. **Calculate** the ratios g_1/g_0 at temperatures of 12 K and 25 °C for an absorption peak at 3953.8 cm^{-1}. The occupation number for a given level is proportional to the distribution ratio at that level.

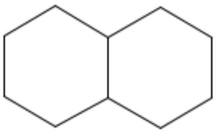
Problem 8. Quantum chemistry of aromatic molecules

The behavior of π-electrons is of paramount importance for understanding the reactivity and photophysical properties of aromatic compounds. In the electronic theory of organic chemistry, the electronic structure is considered to be a superposition of several 'resonating' electronic states.

1. Following the example below, **draw** all possible resonance structures for the compounds listed below. It should be noted that the positions of the atoms (nuclei) must remain unchanged. As only the skeletons of the structures are shown, add bonds as appropriate according to the chemical formulae. Do not include resonance structures with separated charges or unpaired electrons.

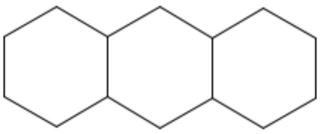


(a)



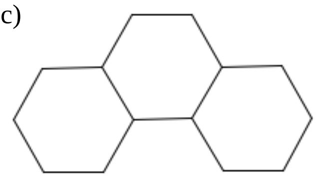
$C_{10}H_8$

(b)



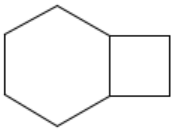
$C_{14}H_{10}$

(c)



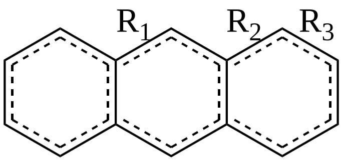
$C_{14}H_{10}$

(d)

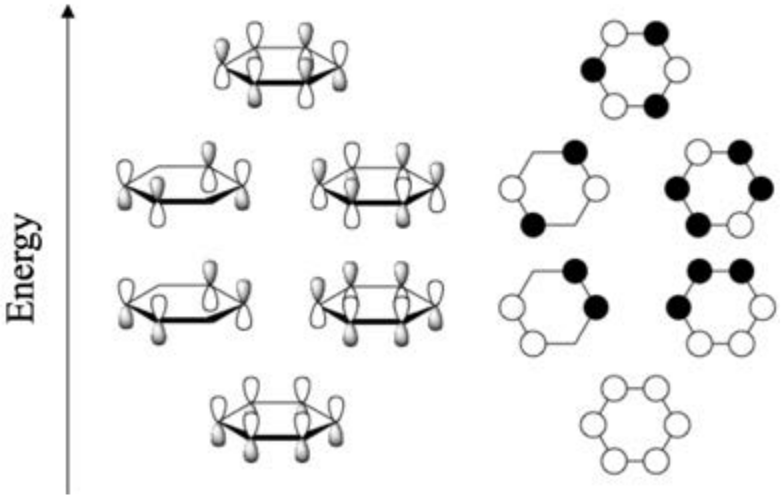


C_8H_6

2. In real benzene, all carbon–carbon bonds have the same bond length (1.399 Å), which means that the two cyclohexatriene resonance structures are extremes, and their superposition represents the real molecule. With this in mind, we will consider the bond lengths R_1, R_2, and R_3 in anthracene. Assuming that R_S is the typical length of a carbon–carbon single bond (1.53 Å) and R_D that of a typical C=C double bond (1.34 Å), **arrange** R_S, R_D, R_1, R_2, and R_3 in order of length.



Following Questions are optional:
The properties of molecules are governed by their wavefunctions. Although resonance structures are useful for discussing various physical properties, it is difficult to use them to predict reactivity. The frontier orbital theory, proposed by Fukui and co-workers, is suitable for discussing reactivity based on molecular orbitals. For example, the six molecular orbitals of benzene are shown in the figure below.

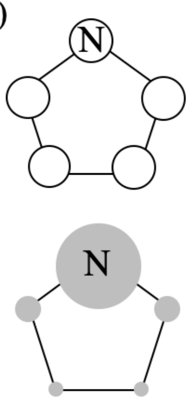


The π-orbitals consist of p-orbitals perpendicular to the molecular plane of each atom (left panel); the white and black parts of each correspond to positive and negative values of the wavefunction. The right panel shows the same information more simply.

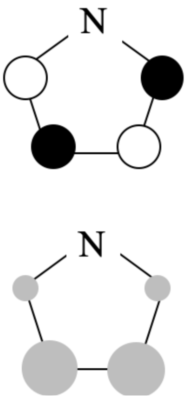
3. **Give** the number of orbitals occupied by π-electrons in benzene, naphthalene, and pyrrole.

4. Based on the following facts, **choose** the right pyrrole HOMO (highest occupied molecular orbital) from the options (a)-(c) below. The positive and negative values of wave functions are represented with white and black in the upper panel. In the lower panel, the circles on the atoms are drawn with a size proportional to the electron density.
   - The reaction readily takes place at the position with the largest electron density in the HOMO.
   - The electrophilic substitution reaction of pyrrole occurs faster at the 2 position than at the 3 position.

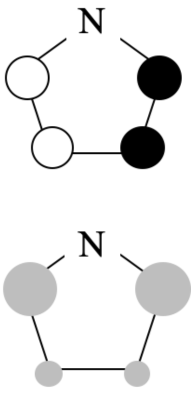
(a)



(b)



(c)



5. **Arrange** these orbitals in order of their energy, from lowest energy to highest energy. The diagram of benzene can be used as a guide.

Problem 9. Protic ionic liquids

Water undergoes autoprotolysis according to:

$$2\ H_2O \rightleftarrows H_3O^+ + OH^- \qquad (1)$$

The product of the concentration of dissociated ions is constant and known as the autoprotolysis equilibrium constant.

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14} \quad (25\ °C) \qquad (2)$$

The negative decadic logarithm of the concentration of H_3O^+ is known as the pH value, which is used as a scale of the acidity of an aqueous solution:

$$pH = -\log_{10}[H_3O^+] \qquad (3)$$

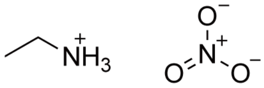
When the concentration of the cations and the anions generated by autoprotolysis is the same, the solution is said to be neutral. In the case of water at 25 °C, the neutral condition, *i.e.*, $[H_3O^+] = [OH^-]$, holds when pH = 7.

1. Autoprotolysis also occurs in liquids other than water. For example, the autoprotolysis equilibrium constant of methanol is $10^{-16.7}$ at 25 °C.

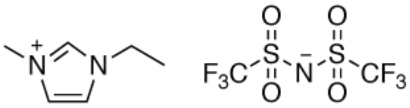
1-1. **Write** the chemical equation for the autoprotolysis of methanol.

1-2. **Calculate** the concentration of the cation of methanol under neutral conditions at 25 °C.

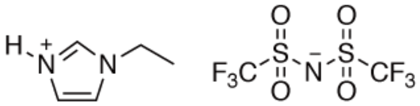
Substances composed of ionic bonds, such as sodium chloride, usually exist in solid form at room temperature. In 1914, ethylammonium nitrate was reported as a unique salt that exists as a liquid even at room temperature. Such salts are known as ionic liquids, and these have attracted considerable attention recently.



1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (hereafter denoted as CM^+/B^-) is a commonly used ionic liquid.



1-Ethylimidazolium bis(trifluoromethanesulfonyl)imide (hereafter denoted as CH^+/B^-), which has a similar structure to CM^+/B^- except that the methyl group on the imidazole ring is replaced by a proton, is also an ionic liquid.



CH^+/B^- shows an equilibrium that is similar to autoprotolysis:

$$CH^+/B^- \rightleftarrows C + HB \qquad (4)$$

$$K_s = [C][HB] \qquad (5)$$

To determine the K_s of CH^+/B^-, electrochemical measurements have been conducted (Figure 1). Using CH^+/B^- as a solvent, a 0.35 mol L^{-1} bis(trifluoromethanesulfonyl)imide solution (henceforth: HB solution) and a 3.2 mol L^{-1} 1-ethylimidazole solution (henceforth: C solution) were prepared.

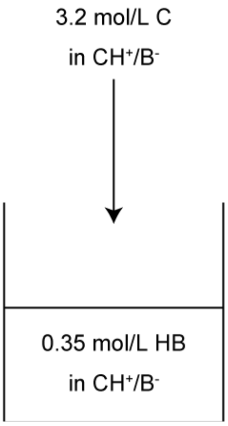


Figure 1. Schematic illustration of the experimental setup.

7.3 mL of the HB solution was titrated with the C solution, and the electromotive force was measured during the titration using an electrode that responds to HB. The obtained electric voltage, E_i, can be expressed by:

$$E_i = E^\circ + RT/F \ln[\mathrm{HB}] \tag{6}$$

The resulting electric voltages as a function of the amount of the C solution added, V_i, are shown in Figure 2.

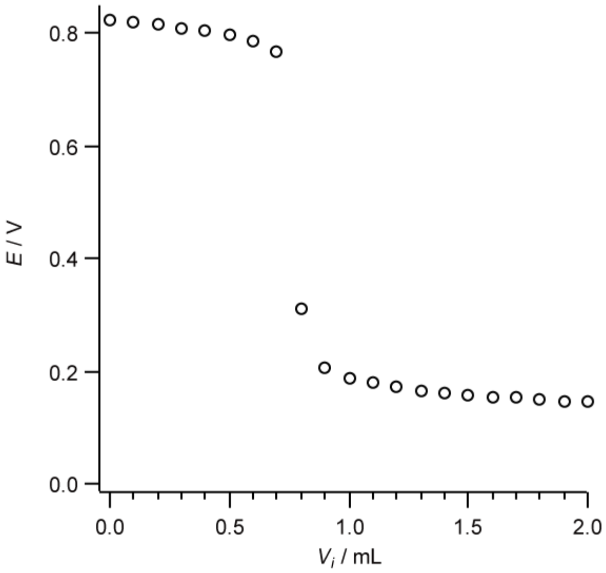


Figure 2. Electric voltages during the titration of the HB solution as a function of the amount of the C solution added (V_i).

The total concentration of protons, C_H, and the total concentration of imidazole, C_{im}, can be expressed by:

$$C_H = [\mathrm{HB}] + [\mathrm{CH}^+] \tag{7}$$

$$C_{im} = [\mathrm{C}] + [\mathrm{CH}^+] \tag{8}$$

In the following problems, assume that the temperature of the solutions is 25 °C.

2. First, let us consider the case where there is an excess of HB. At the point of neutralization, the observed electric voltage changes drastically. This indicates that K_s is very small, and therefore almost all C added prior to the point of neutralization is protonated ($[\mathrm{C}] << [\mathrm{CH}^+]$).

2-1. Consider the case where the initial concentration of HB solution is $[\mathrm{HB}]_0$ (= 0.35 mol L^{-1}), the concentration of C solution is $[\mathrm{C}]_0$ (= 3.2 mol L^{-1}), the concentration of CH^+ originating from the solvent is $[\mathrm{CH}^+]_{\mathrm{sol}}$, and the volume of HB solution before the titration is V_0 (= 7.3 mL). **Write** an expression for C_H and C_im in terms of V_0, V_i, $[\mathrm{HB}]_0$, $[\mathrm{C}]_0$, and $[\mathrm{CH}^+]_{\mathrm{sol}}$. Assume that $[\mathrm{CH}^+]_{\mathrm{sol}}$ does not change during the titration.

2-2. When 0.50 mL of the C solution was added, E_i was 0.796 V. **Calculate** the value of $E°$. Note that the concentration of HB can be approximated as $[\mathrm{HB}] = C_\mathrm{H} - C_\mathrm{im}$.

To analyze the obtained result, Figure 2 is replotted with $(V_0+V_i)\exp(\pm E_iF/RT)$ as the vertical axis (Figure 3).

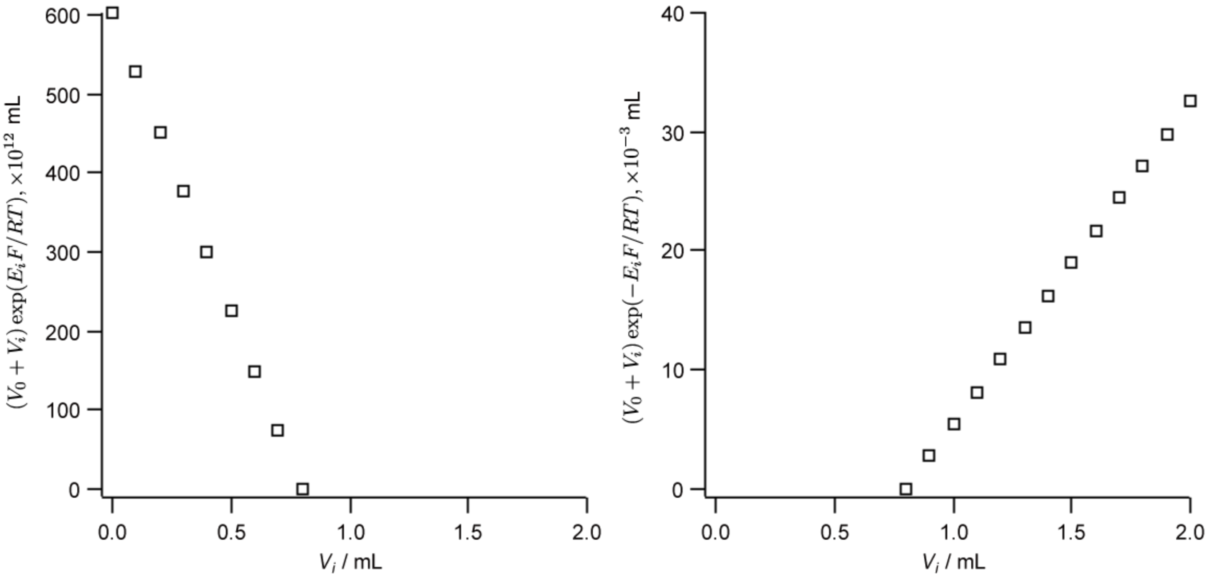


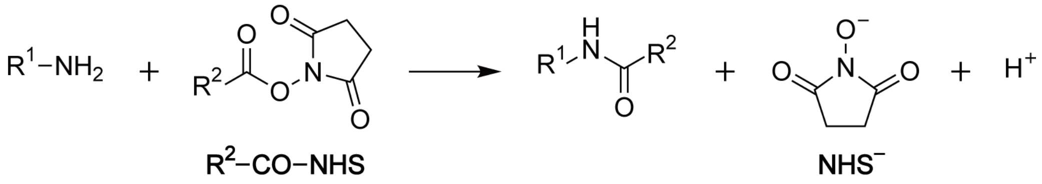
Figure 3. Replotted graphs of Figure 2.
(Left) Before the point of neutralization. (Right) After the point of neutralization.

3. When the C solution is added beyond the point of neutralization, there is an excess of C. In this case, almost all the protons bind to C, and there are few protons that exist in the form of HB.

3-1. **Write** an expression for [HB] beyond the point of neutralization in terms of C_H, C_im, and K_s. Assume that $C_\mathrm{H} = [\mathrm{HB}] + [\mathrm{CH}^+] \simeq [\mathrm{CH}^+]$, which holds when there is an excess of C.

3-2. The slope of $(V_0+V_i)\exp(-E_iF/RT)$ as a function of V_i is 0.0271 beyond the point of neutralization. **Calculate** K_s.

Let us consider how to control the reaction rate of the following chemical reaction.



(S1)

An amide bond is produced by the reaction between the amine and the active ester. In the following problems, assume that all of the produced *N*-hydroxysuccinimide (pK_a = 6.0 in water) exists in the deprotonated form (NHS^-). Ignore the degradation reaction of the active ester. The temperature of the solutions is 25 °C.

First, let us consider reaction S1 in a buffered aqueous solution. In an aqueous solution, the acid–base equilibrium of $R^1–NH_2$ is expressed by:

$$R^1–NH_3^+ + H_2O \rightleftarrows R^1–NH_2 + H_3O^+ \quad (9)$$

$$K_a = [R^1–NH_2]\,[H_3O^+] / [R^1–NH_3^+] = 10^{-9.27} \quad (10)$$

The reaction rate of S1 is expressed as a second-order reaction:

$$d[–NH–CO–]/dt = k\,[R^1–NH_2][R^2–CO–NHS] \quad (11)$$

The variation of [–NH–CO–] over time is obtained by integrating eq. 11, which gives:

$$[–NH–CO–] = ([R^1–NH_2]_0 + [R^1–NH_3^+]_0)(1 - \exp(-k[R^2–CO–NHS]\,f_a\,t)\,) \quad (12)$$

$[R^1–NH_2]_0$ and $[R^1–NH_3^+]_0$ represent the initial concentrations of $R^1–NH_2$ and $R^1–NH_3^+$, respectively, while f_a represents the ratio of the deprotonated form of the amine, which is defined by:

$$f_a = [R^1–NH_2] / ([R^1–NH_2] + [R^1–NH_3^+]) \quad (13)$$

When the reaction occurs in a buffered aqueous solution, f_a remains constant during the reaction because the pH of the solution is constant.

4. The reaction progress in a mixture of 20 μmol of $R^1–NH_2$ in 10 mL of the buffer solution and 200 μmol of $R^2–CO–NHS$ in 10 mL of the buffer solution is monitored via the absorption of NHS^- in the ultraviolet region. In this case, the concentration of $R^2–CO–NHS$ is regarded constant during the reaction, because it is significantly higher than that of $R^1–NH_2$ (pseudo-first-order reaction). **Reaction S1 proceeds only for the deprotonated amine, $R^1–NH_2$. The protonated amine, $R^1–NH_3^+$, does not react with the active ester.**

4-1. **Calculate** the time at which half of the added $R^1–NH_2$ will have reacted when $k' = k[R^2–CO–NHS] = 5.0 \times 10^{-2}\ s^{-1}$ and pH = 9.27.

4-2. In a differently buffered solution, the time at which one-third of the added $R^1–NH_2$ has reacted is 500 s when $k' = 5.0 \times 10^{-2}\ s^{-1}$. **Calculate** the pH of the buffer solution in this case.

Then, let us consider reaction S1 in the ionic liquid CM^+/B^-. In CM^+/B^-, the acid–base equilibrium of $R^1–NH_2$ is expressed as follows:

$$R^1–NH_3^+ + B^- \rightleftarrows R^1–NH_2 + HB \quad (14)$$

$$K_a^A = [R^1–NH_2]\,[HB] / [R^1–NH_3^+] = 10^{-16.40} \quad (15)$$

The reaction rate of S1 is expressed as a second-order reaction:

$$d[–NH–CO–]/dt = k_I\,[R^1–NH_2][R^2–CO–NHS] \quad (16)$$

5. As shown in Q4, to control the reaction rate of S1, the ratio of $[R^1–NH_2]$ should be set to the appropriate value by adjusting the proton concentration in the solution. However, the ionic liquid CM^+/B^- does not contain a proton. To solve this problem, let us use the ionic liquid CH^+/B^-, which was considered in Q2 and Q3, as a proton source for CM^+/B^-. The acid–base equilibrium of CH^+ in CM^+/B^- can be expressed by:

$$CH^+ + B^- \rightleftarrows C + HB \quad (17)$$

$$K_a^C = [C]\,[HB] / [CH^+] = 10^{-14.90} \quad (18)$$

5-1. **Calculate** the [HB] of a 6.00×10^{-3} mol L^{-1} CH^+/B^- solution dissolved in the ionic liquid CM^+/B^-.

5-2. A $R^1–NH_2$ solution is prepared using the solution from Q5-1 as the solvent. The [HB] of the solution of 100 μmol $R^1–NH_2$ in 10 mL of the solvent is 5.39×10^{-17} mol L^{-1}. **Calculate** the concentrations of CH^+, C, $R^1–NH_3^+$, and $R^1–NH_2$.

As shown in Q5-2, most of the protons added as CH^+ are transferred to R^1–NH_2 and exist in the form of R^1–NH_3^+. Similarly, the protons produced in reaction S1 also bind to R^1–NH_2. As the resulting chemical species, R^1–NH_3^+, does not react with the active ester, the reaction rate decreases as the reaction proceeds.

5-3. Reaction S1 is started once 100 μmol of R^2–CO–NHS have been dissolved in the solution from Q5-2. **Calculate** the concentrations of HB, CH^+, C, R^1–NH_3^+, and R^1–NH_2 when the concentration of R^2–CO–NHS become 8.00×10^{-3} mol L^{-1}.

5-4. To avoid a decrease in the reaction rate, the concentration of HB should remain constant. When CH^+/B^- and C are dissolved together, the concentration of HB is determined by the ratio of the concentrations of C and CH^+. **Express** [HB] in terms of [C], $[CH^+]$, and K_a^C.

A buffer solution is prepared by adding the appropriate amount of C to 0.10 mol L^{-1} of CH^+/B^- solution using CM^+/B^- as the solvent. The reaction progress of a mixture of 20 μmol R^1–NH_2 in 10 mL of the buffer solution and 200 μmol of R^2–CO–NHS in 10 mL of the buffer solution is monitored. The variation in [–NH–CO–] over time can be expressed by:

$$[\text{–NH–CO–}] = ([R^1\text{–}NH_2]_0 + [R^1\text{–}NH_3^+]_0)(1 - \exp(-k_I' f_a\, t)) \qquad (19)$$

5-5. The time at which one third of the added R^1–NH_2 will have reacted is 2000 s when $k_I' = k_I[R^2\text{–CO–NHS}] = 8.0 \times 10^{-4}\ s^{-1}$. **Calculate** the concentration of C in the buffer solution.

[Note] The reaction control technique explained above has already been applied to the condensation of the two polymers shown in Figure 4. As a result, high-strength gels with homogeneous network structures were prepared from both aqueous solutions and ionic liquids (for an example, see: T. Sakai *et al.*, *Macromolecules* **2008**, *41*, 5379).

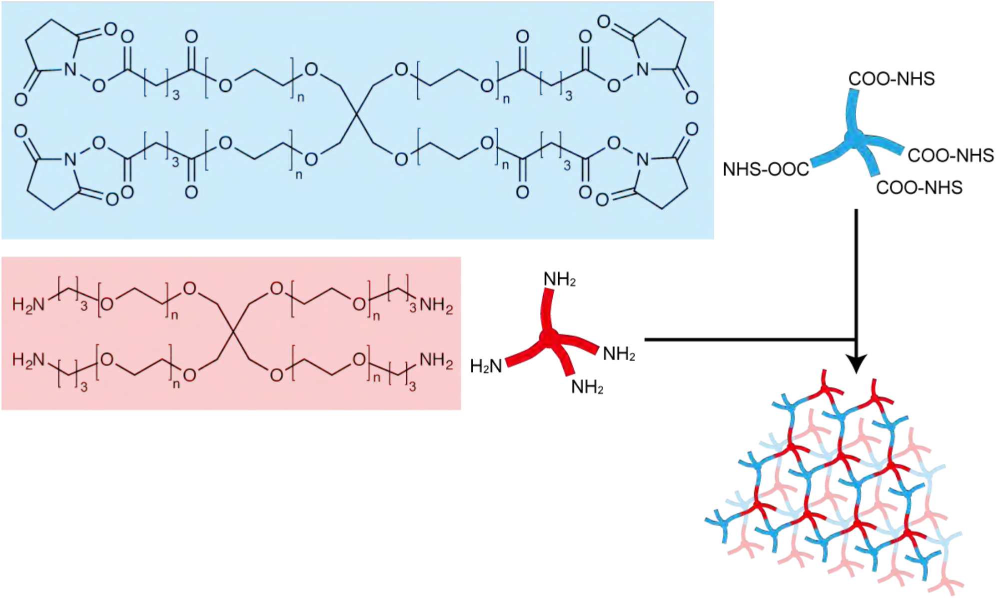


Figure 4. Conceptual illustration of the controlled synthesis of high-strength gels.

Problem 10. The Yamada universal indicator

In this problem, assume that the optical path length of the cell is 1.0 cm. Ignore the absorption of the cell and the solvent.

1. The acid dissociation constant of bromothymol blue (BTB) is $10^{-7.10}$. The absorbance values of 200 μmol L^{-1} BTB aqueous solutions with different pH values (2.00, 12.00) were measured, and the results are shown in Table 1.

Table 1. Absorbance values of 200 μmol L^{-1} BTB solutions

Wavelength	420 nm	501 nm	520 nm
pH = 2.00	1.74	0.70	0.36
pH = 12.00	0.60	0.70	1.06

1-1. **Calculate** the molar absorption coefficients of the protonated/deprotonated forms of BTB at 420 nm, 501 nm, and 520 nm.

1-2. At a certain pH value, the absorbance values of an aqueous solution containing a small amount of BTB at 420 nm and 520 nm were 1.13 and 0.52, respectively. **Calculate** the pH of this aqueous solution.

1-3. The aqueous solution used in Q1-2 was diluted 5 times using hydrochloric acid with pH = 1. **Calculate** the absorbance value of the diluted solution at 501 nm.

1-4. The aqueous solution used in Q1-2 was diluted 5 times using aqueous sodium hydroxide with pH = 12. **Calculate** the absorbance value of the diluted solution at 501 nm.

To estimate the pH of a solution using indicators, appropriate indicators that show a clear color change in the target pH region should be used. Universal indicators have been developed as easy-to-use indicators. Universal indicators can be prepared by mixing several kinds of indicators so that the resulting mixture shows color changes over a wide pH region. As a representative universal indicator, let us consider the Yamada universal indicator, which was developed by a Japanese researcher, Shinobu Yamada, in 1933.

The components of the Yamada universal indicator, its color under various pH conditions, the molar absorption coefficients of each indicator, and the acid dissociation constants of each indicator are summarized in Tables 2, 3, 4, and 5, respectively.

Table 2. Components of the Yamada universal indicator **dissolved in 100 mL ethanol**

Indicators	Molecular weight	Weight [mg]
Thymol blue (TB)	466.6	5.00
Methyl red (MR)	269.3	12.5
Bromothymol blue (BTB)	624.4	50.0
Phenolphthalein (PP)	318.3	100.0

Table 3. Color of the Yamada universal indicator under various pH conditions

pH	– 3	3 – 6	6 – 8	8 – 11	11 –
Color	Red	Yellow	Green	Blue	Purple

Table 4. Molar absorption coefficients of each indicator (unit: mol^{-1} L cm^{-1})

Wavelength [nm]	400	450	500	550	600	650
TB, H_2A	5500	2500	6000	18000	1500	0
TB, HA^-	6000	7000	3000	500	0	0
TB, A^{2-}	3500	1500	3500	10000	17500	2500
MR, HA^-	1000	10000	35000	35000	1500	0
MR, A^{2-}	15500	16000	4000	500	0	0
BTB, HA^-	7500	9000	3500	500	0	0
BTB, A^{2-}	5000	1000	3500	10000	20000	10000
PP, HA^-	0	0	0	0	0	0
PP, A^{2-}	1000	1000	6000	21000	1000	0

Table 5. Acid dissociation constants of each indicator
(In this problem, ignore all acid dissociation constants except for these.)

Indicator	TB	MR	BTB	PP
pK_a	$pK_{a1} = 1.7$, $pK_{a2} = 8.9$	5.1	7.1	9.7

2. The Yamada universal indicator (1.0 mL) was added to aqueous solutions (29.0 mL) with various pH values, and the absorbance of these solutions was measured. The measured absorbance values and the colors of the solutions are shown in Table 6. **Calculate** the pH of solutions (1), (2), and (3) after the addition of the Yamada universal indicator up to one decimal place.
   Note that under each pH condition, only one of the four indicators exhibits a drastic change in the ratio of its protonated/deprotonated forms by the slight change of its pH value.

Table 6. Measured absorbance values and colors of the solutions

	Color	Wavelength [nm]					
		400	450	500	550	600	650
pH = 1.0	Red	0.236	0.407	0.655	0.609	0.028	0.000
(1)	Yellow	0.323	0.455	0.460	0.352	0.018	0.002
(2)	Green	0.435	0.440	0.176	0.121	0.179	0.089
(3)	Blue	0.466	0.360	0.645	1.979	0.673	0.275
pH = 12.0	Purple	0.490	0.384	0.793	2.498	0.701	0.276

Problem 11. Silver electroplating

Silver electroplating, in which silver is deposited on a metal surface, has been used to decorate objects and to increase their electrical conductivity. In silver electroplating, usually an aqueous alkaline solution containing $\mathrm{Ag^+}$ and $\mathrm{CN^-}$ is used. The metal to be plated is used as the cathode, and silver ions are deposited on the metal surface by reductive deposition. Pure silver is used as the anode, from which silver ions are supplied to the solution by oxidative dissolution. The half reaction and standard electrode potential $E°$ of the reductive deposition/oxidative dissolution of $\mathrm{Ag^+}$ are as follows:

$$\mathrm{Ag^+ + e^- \rightleftharpoons Ag(s)} \qquad E° = 0.799\ \mathrm{V}$$

In the solution, $\mathrm{Ag^+}$ forms several kinds of complexes with $\mathrm{CN^-}$ and $\mathrm{OH^-}$. The complex formation reactions and formation constants are as follows:

$$\begin{array}{ll}
\mathrm{Ag^+ + CN^- + OH^- \rightleftharpoons Ag(OH)(CN)^-} & K_{\mathrm{OHCN}} = 10^{13.20} \\
\mathrm{Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-} & \beta_2 = 10^{20.40} \\
\mathrm{Ag^+ + 3CN^- \rightleftharpoons Ag(CN)_3^{2-}} & \beta_3 = 10^{21.40} \\
\mathrm{Ag^+ + 4CN^- \rightleftharpoons Ag(CN)_4^{3-}} & \beta_4 = 10^{20.80}
\end{array}$$

where the overall formation constants β_i are defined as $\beta_i = \frac{[\mathrm{Ag(CN)_i^-}]}{([\mathrm{Ag^+}][\mathrm{CN^-}]^{\mathrm{i}})}$.

Answer the following questions. Unless otherwise noted, $[\mathrm{CN^-}] = [\mathrm{OH^-}] = 1.00\ \mathrm{M}$, and the total concentration of Ag-related dissolved species is 1.00 mM. Use the absolute temperature $T = 298.2$ K.

1. **Write** the five Ag-related dissolved species in this solution in order of concentration. **Calculate** the concentration of the species with the highest concentration.

   ☐ > ☐ > ☐ > ☐ > ☐

2. **Write** the half reaction in which the Ag-related dissolved species with the highest concentration in Q1 is reduced to Ag(s). **Calculate** the $E°$ of the half reaction.

3. If $[\mathrm{CN^-}]$ varies from 1.00 M, the relative order of the species in Q1 will also vary. **Calculate** the concentration range of $[\mathrm{CN^-}]$ within which the relative order in Q1 holds.

4. **Calculate** the equilibrium potential of the cathode, assuming that the cathode surface is covered with Ag(s).

5. The reductive deposition reaction of silver competes with the hydrogen evolution reaction (HER). The potentials at which the HER occurs depend on the pH of the solution; the higher the pH, the more negative the potentials for the HER. By comparing the equilibrium potential calculated in Q4 with that for the HER, **calculate** the lower pH limit above which the reductive deposition reaction of silver is more thermodynamically favorable than the HER.

6. Because $\mathrm{HCN(g)}$ is highly toxic, the evolution of this gas should be minimized, even when using a fume hood. **Calculate** the pH requirements for the solution to keep the equilibrium partial pressure of $\mathrm{HCN(g)}$ below 10 ppm (= $10^{-5.0}$ bar). Use the following equilibrium equations for the calculation.

$$\mathrm{HCN(g)} \rightleftharpoons \mathrm{HCN(aq)} \qquad K_\mathrm{H} = 10^{1.0}$$
$$\mathrm{HCN(aq)} \rightleftharpoons \mathrm{H^+} + \mathrm{CN^-} \qquad K_a = 10^{-9.2}$$

Problem 12. How does CO_2 in the atmosphere affect the pH value of seawater?

Let us consider the chemical equilibrium of carbonic acid in ocean acidification, which is caused by an increase in the concentration of carbon dioxide in the atmosphere. Use the following equilibrium equations and constants:

$$\begin{array}{lll} \mathrm{CO_2(g)} & \rightleftharpoons \mathrm{CO_2} & K_{\mathrm{gas}} = 10^{-1.46} \\ \mathrm{CO_2 + H_2O} & \rightleftharpoons \mathrm{H_2CO_3} & K_{\mathrm{hyd}} = 10^{-2.70} \\ \mathrm{H_2CO_3} & \rightleftharpoons \mathrm{H^+ + HCO_3{}^-} & K_{\mathrm{a1}} = 10^{-3.65} \\ \mathrm{HCO_3{}^-} & \rightleftharpoons \mathrm{H^+ + CO_3{}^{2-}} & K_{\mathrm{a2}} = 10^{-10.33} \\ \mathrm{H_2O} & \rightleftharpoons \mathrm{H^+ + OH^-} & K_{\mathrm{w}} = 10^{-14.00} \end{array}$$

where (g) denotes a species in the gaseous state, and all species other than $\mathrm{CO_2(g)}$ and $\mathrm{H_2O}$ are dissolved in an aqueous solution. Let the current value of the molar fraction of carbon dioxide in the atmosphere, $x_{\mathrm{CO_2}}$, be 410 ppm (= 410 × 10^{-6} bar).

1. When pure water is left exposed to the atmosphere, it absorbs carbon dioxide from the atmosphere, which changes its pH. **Calculate** the pH of water in equilibrium with the atmosphere using the following charge balance equation:

$$[\mathrm{H^+}] = [\mathrm{OH^-}] + [\mathrm{HCO_3{}^-}] + 2\left[\mathrm{CO_3{}^{2-}}\right]$$

2. To the water in equilibrium with the atmosphere in Q1, a strong base or strong acid was added such that the pH changed by ±1 ($\Delta\mathrm{pH} = \pm 1$). The solution was then left exposed to the atmosphere again. What is the change in the amount of absorbed carbon dioxide relative to that before the addition? **Choose** the pH change for each scenario from the following Options. Assume that there is no change in the liquid volume due to the acid/base addition.

   (a) Strong base ($\Delta\mathrm{pH} = +1$)
   (b) Strong acid ($\Delta\mathrm{pH} = -1$)

   Options
   (1) The amount of absorbed carbon dioxide increases to more than double the initial value.
   (2) The amount of absorbed carbon dioxide decreases to less than half the initial value.
   (3) The magnitude of the increase or decrease is less than described in Options (1) and (2).

3. Currently, $x_{\mathrm{CO_2}}$ continues to rise. A report has predicted that $x_{\mathrm{CO_2}}$ will exceed 800 ppm by 2070 (*cf.* IPCC RCP 8.5). **Calculate** the pH of water in equilibrium with the atmosphere if $x_{\mathrm{CO_2}}$ were twice its current value ($x_{\mathrm{CO_2}} = 2 \times 410 = 820$ ppm) and **evaluate** the pH shift relative to the pH found in Q1 where the current $x_{\mathrm{CO_2}}$ value was used.

As $x_{\mathrm{CO_2}}$ rises, the oceans, like pure water, become more acidic. The current pH of the oceans is 8.05 on average, although it varies spatially and temporally. Compared to the pre-industrialization value in the 18th century, the current pH of the oceans has decreased by 0.1. If the pH decreases a further 0.2 to 7.85 in the future, the decrease in $\left[\mathrm{CO_3{}^{2-}}\right]$ will result in $\mathrm{CaCO_3}$ (aragonite), which is a component of the shells of corals and phytoplankton, being dissolved at low temperatures, causing severe damage to the marine biota. Let us estimate how much a rise in $x_{\mathrm{CO_2}}$ would reduce pH.

4. First, let us estimate the ocean acidification due to the rise in $x_{\mathrm{CO_2}}$, ignoring chemical equilibria other than those of carbonic acid. A variety of ions are dissolved in the ocean. The difference in the concentration of the cations and anions originating from strong electrolytes, $C_{\mathrm{C-A}}$, appears as a constant in the charge balance equation.

$$[\mathrm{H^+}] + C_{\mathrm{C-A}} = [\mathrm{OH^-}] + [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}]$$

Calculate the pH shift when $x_{\mathrm{CO_2}}$ increases from 410 to 820 ppm, with $C_{\mathrm{C-A}} = 0.72$ mM.

5. In real seawater, chemical equilibria other than those of carbonic acid affect this pH shift. Let us calculate the pH shift taking into account the following ion-pair formation constant for $\mathrm{MgCO_3}$ (dissolved species):

$$\mathrm{Mg^{2+}} + \mathrm{CO_3}^{2-} \rightleftharpoons \mathrm{MgCO_3} \qquad K_\mathrm{f} = 10^{2.88}$$

The charge balance equation can be written as:

$$2[\mathrm{Mg^{2+}}] + [\mathrm{H^+}] + C_{\mathrm{C-A}} = [\mathrm{OH^-}] + [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}]$$

where $C_{\mathrm{C-A}} = -105.0$ mM. Use $C_{\mathrm{Mg}} = 53.0$ mM as the total concentration of Mg-related species. **Calculate** the pH when $x_{\mathrm{CO_2}}$ changes from 410 to 820 ppm. It may be helpful to use an approximation, $(1-x)^{-1} \sim 1 + x$, for $x \ll 1$. Can corals survive?

Let us consider the meaning of the pH shift evaluated in Q3 and Q4 using a virtual weak acid HA which dissociates as follows:

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

with the acid dissociation constant $K_\mathrm{a} = 10^{-3.00}$ (note that this constant is different from that of carbonic acid). A solution is prepared using a given concentration of HA, C_{HA}, and a given concentration of its conjugate base salt NaA, C_{NaA}. The pH of the solution depends on these concentrations. The dependence of the pH on $\mathrm{p}C_{\mathrm{HA}}(= -\log_{10} C_{\mathrm{HA}})$ and $\mathrm{p}C_{\mathrm{NaA}}(= -\log_{10} C_{\mathrm{NaA}})$ is shown as a contour map below. A doubling in C_{HA} corresponds to a –0.30 shift of $\mathrm{p}C_{\mathrm{HA}}$ to the left in this contour map.

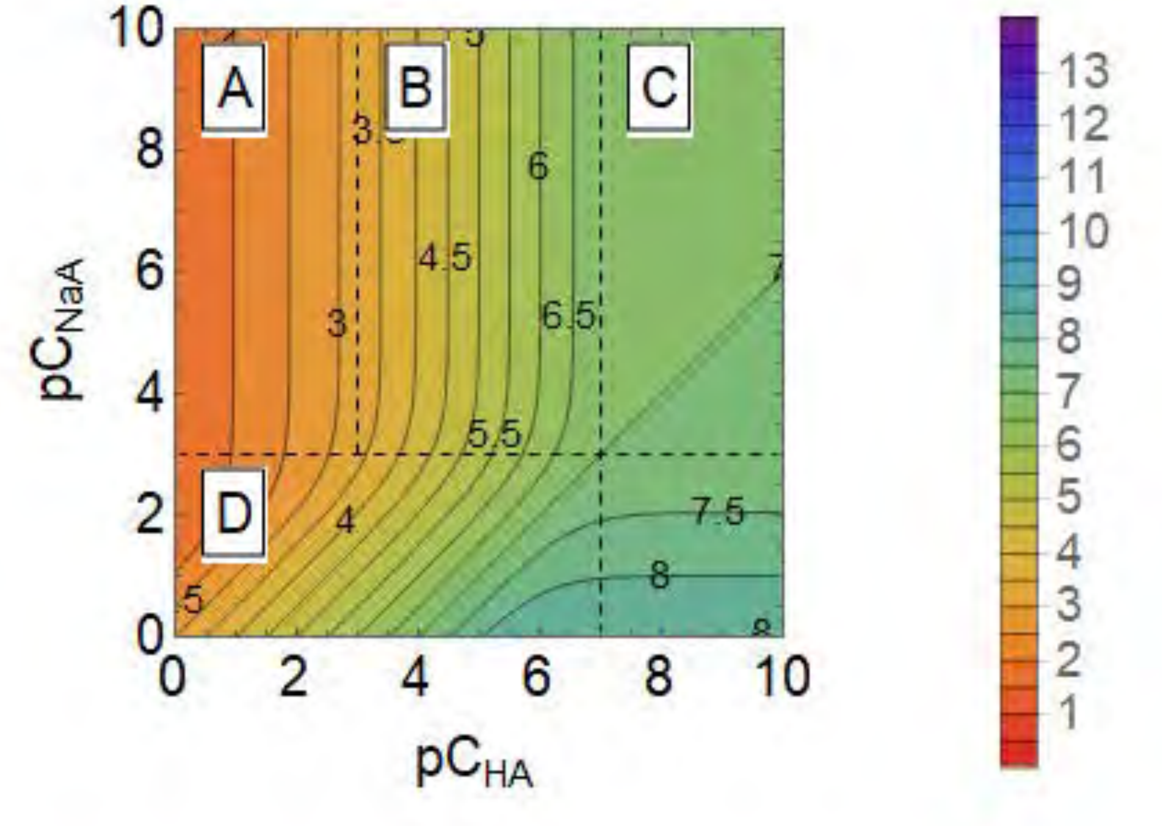


Fig. 1. Contour map of pH for an HA/NaA solution.

6. In the situation described in Q3, *i.e.*, pure water in equilibrium with the atmosphere, C_{NaA} is ideally zero and can be neglected. In the above contour map, this situation corresponds to either Region A, B, or C, where $\mathrm{p}C_{\mathrm{NaA}}$ is large and the following inequalities for $\mathrm{p}C_{\mathrm{HA}}$ hold:

(Region A) $\mathrm{p}C_{\mathrm{HA}} < \mathrm{p}K_{\mathrm{a}}$
(Region B) $\mathrm{p}K_{\mathrm{a}} < \mathrm{p}C_{\mathrm{HA}} < \frac{\mathrm{p}K_{\mathrm{w}}}{2}$
(Region C) $\frac{\mathrm{p}K_{\mathrm{w}}}{2} < \mathrm{p}C_{\mathrm{HA}}$

Derive analytical solutions for the pH as a function of $\mathrm{p}C_{\mathrm{HA}}$ using the charge balance equation:

$$[\mathrm{H}^+] = [\mathrm{OH}^-] + [\mathrm{A}^-]$$

combined with the above inequalities for each Region. Because doubling C_{HA} corresponds to a –0.30 shift in $\mathrm{p}C_{\mathrm{HA}}$ as described above, the pH shift can be determined from the derived analytical solutions. **Calculate** the pH shift when C_{HA} is doubled for Regions A, B, and C, respectively. The situation in Q3 corresponds to Region ☐. **Fill** in this blank with either A, B, or C.

7. In the solution with pH = 8.05 in Q4, in which we ignored any chemical equilibria other than that of carbonic acid, $HCO_3{}^-$ is the main component among the carbonic-acid-related dissolved species. This solution can be regarded as an aqueous solution of $NaHCO_3$, which corresponds to Region D with a large C_{NaA}, *i.e.*, a small pC_{NaA}, in the contour map. In Region D, the Henderson–Hasselbalch equation holds, in which the equilibrium equation $K_a = \frac{[H^+][A^-]}{[HA]}$ is approximated using $[HA] = C_{HA}$ and $[A^-] = C_{NaA}$. **Calculate** the pH shift using the Henderson–Hasselbalch equation when C_{HA} doubles in Region D.

Problem 13. How to produce sulfuric acid and dilute it without explosion

Japan is a country rich in sulfur resources. Sulfuric acid can be synthesized from sulfide-based mineral resources such as copper sulfide, iron sulfide, and lead sulfide.

1. When a mixture of chalcopyrite ($CuFeS_2$) and silica sand (SiO_2) is melted at high temperature in the presence of oxygen in a blast furnace, sulfur dioxide is generated along with Cu_2S and $FeSiO_3$ (Reaction 1). The Cu_2S obtained in Reaction 1 reacts with oxygen at high temperature to form copper and sulfur dioxide (Reaction 2). **Write** the reaction formulae for Reaction 1 and Reaction 2.

2. **Calculate** how many kg of copper and how many liters of sulfur dioxide (at 25 °C, 1.00 bar) will be obtained from 100 kg of pure chalcopyrite by the process described in Q1. Assume that all the reactions proceed completely and that all gases are ideal gases.

3. Sulfur dioxide is oxidized to sulfur trioxide by air using a catalyst such as vanadium(V) oxide. This oxidation proceeds exothermically, and the reaction reaches an equilibrium state as it is a reversible reaction. Which of the following conditions is most appropriate to increase the production ratio of sulfur trioxide? **Choose** one option from (1) to (4).

   (1) Low temperature / Low pressure
   (2) Low temperature / High pressure
   (3) High temperature / Low pressure
   (4) High temperature / High pressure

4. A mixture of sulfur dioxide (7.00 mol) and oxygen (3.00 mol) is placed in a 50.0 L heat- and pressure-resistant container together with a catalyst. When the container is heated to 350 °C, the pressure increases to 8.60 bar. **Calculate** how many moles of sulfur trioxide are generated in this reaction.

5. The absorption of sulfur trioxide by concentrated sulfuric acid produces fuming sulfuric acid. Subsequent dilution of the fuming sulfuric acid with dilute sulfuric acid can afford the desired concentration of sulfuric acid. **Calculate** how many kg of 60% sulfuric acid are needed to dilute 20.0 kg of 32% fuming sulfuric acid (32% by weight SO_3, 68% H_2SO_4) to obtain 98% sulfuric acid. Assume that the volatilization of the components during the dilution is negligible.

6. 8.0 kg of 98% sulfuric acid is diluted with water to give 60% sulfuric acid. **Calculate** the heat of dilution Q [J] released by this dilution process. Note that when 1 mol of H_2SO_4 is diluted with n mol of H_2O, the heat of dilution Q_0 [J] is expressed by the following formula:

   $$Q_0[J] = \frac{7.47 \times 10^4 \times n}{n + 1.80}$$

   The amount of heat required to raise the temperature of 1 g of water by 1 °C is 4.18 J (1 cal). **Calculate** the increase in temperature that the released heat of dilution Q [J] would cause in 10 kg of water (0 °C).

Problem 14. Hydrolysis of C vs Si and the electronegativity of N vs Cl

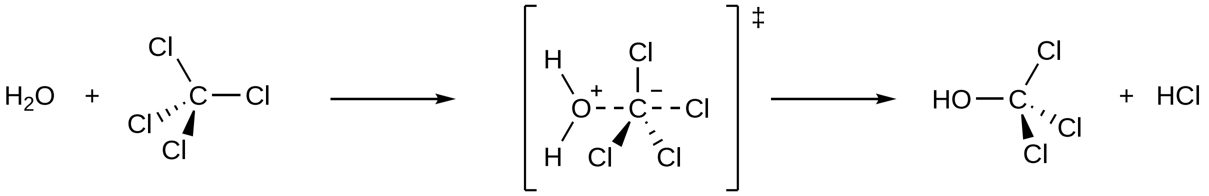
1. Answer the following questions based on the following values of bond-dissociation energies [kJ mol^{-1}]. Assume that the reaction-enthalpy change can be estimated by considering only the bond-dissociation energies of the starting materials and the reaction products.
C–Cl: 335, C–O: 392, O–H: 467, H–Cl: 426, Si–Cl: 451, Si–O: 500, C–H: 413, Si–H: 318.

1-1. Carbon tetrachloride is a stable compound in water, while silicon tetrachloride undergoes facile hydrolysis in water. For reactions (1) and (2) below, which are the initial steps of hydrolysis, **calculate** ΔH [kJ mol^{-1}], which can be estimated based on the bond dissociation energies.

(1) $CCl_4 + H_2O \rightarrow CCl_3OH + HCl$
(2) $SiCl_4 + H_2O \rightarrow SiCl_3OH + HCl$

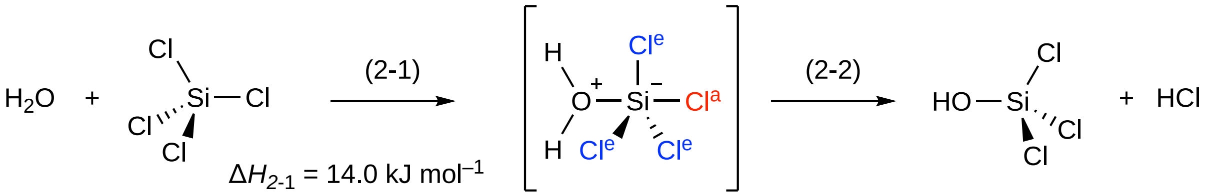
In Q1-1, it cannot be anticipated whether the reaction would proceed smoothly based on only the enthalpy change of the bond-dissociation energies between the reaction substrates and the reaction products. The difference in reactivity between carbon tetrachloride and silicon tetrachloride described in Q1-1 can be explained by the one-step reaction in the carbon case and the multi-step reaction in the silicon case.

(1)



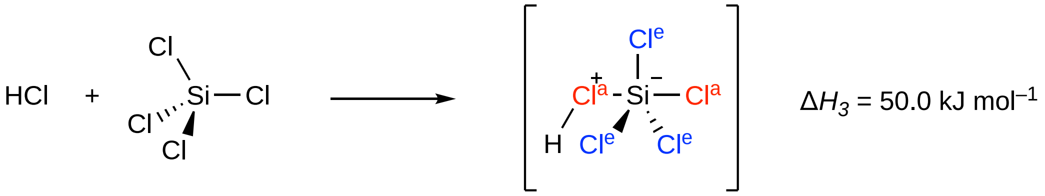
transition state

(2)

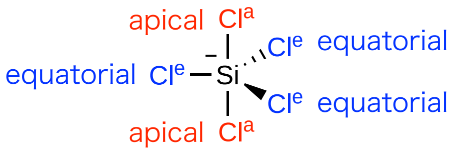


intermediate **A**

(3)



Equation (1) is a one-step reaction that requires a very large activation energy because its transition state involves a penta-coordinated carbon species. Equation (2) is a two-step reaction through an intermediate, which is a penta-coordinated silicon species. For example, as shown in equation (3), a penta-coordinated silicon compound known as a silicate should be generated by the reaction of silicon tetrachloride with hydrogen chloride. The molecular structure of the penta-coordinated silicon compound exhibits a trigonal bipyramidal geometry with a silicon atom at the center and a bonding atom at each vertex of the trigonal bipyramidal skeleton.

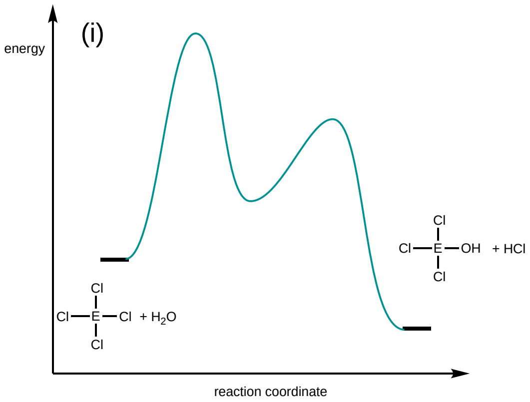


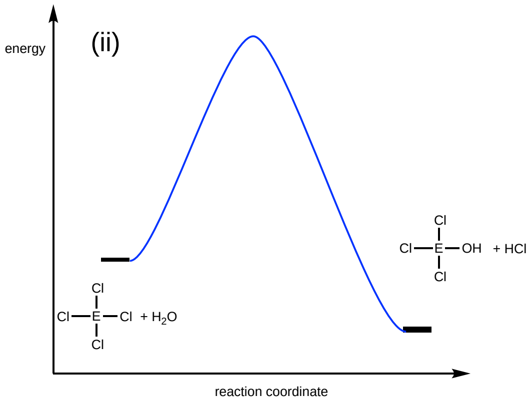
geometry of pentachlorosilicate $SiCl_5^-$,
penta-coordinated silicon species

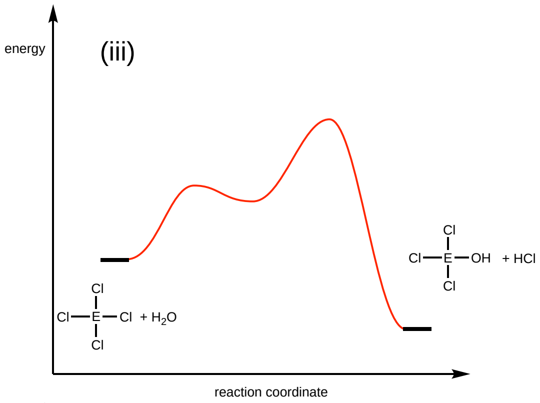
In this intermediate, the bond dissociation energies of the atoms located at the two vertices above and below silicon (apical positions) differ from those of the atoms located at the three vertices that form the triangle centered on silicon (equatorial positions). Assume that the bond-dissociation energies of the equatorial Si–Cl bonds (BE(Si–Cl^e)) are all equal, and that the bond-dissociation energies of the apical Si–Cl bonds (BE(Si–Cl^a)) are also equal. The bond-dissociation energy between the penta-coordinated silicon and the oxygen atom of the apical H_2O molecule is 400 kJ mol^{-1}, and the changes in the bond-dissociation energies of the O–H and Cl–H bonds upon coordination of the H_2O and HCl molecules to the silicon atom to form the corresponding silicates are negligible.

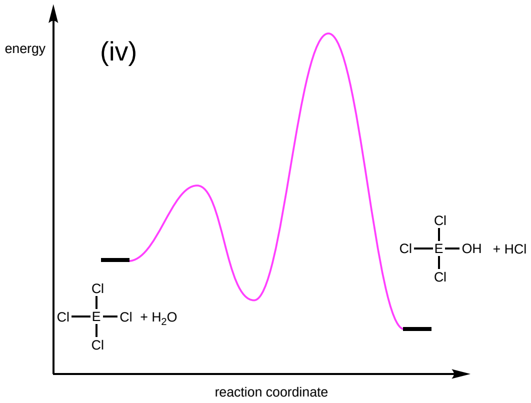
1-2. Provided that $\Delta H_{2\text{-}1}$ in Eq.(2-1) is 14.0 kJ mol^{-1} and ΔH_3 in Eq.(3) is 50.0 kJ mol^{-1}, **calculate** the bond-dissociation energies BE(Si–Cl^a) and BE(Si–Cl^e) between the silicon atom and chlorine atom at the apical and equatorial positions, respectively.

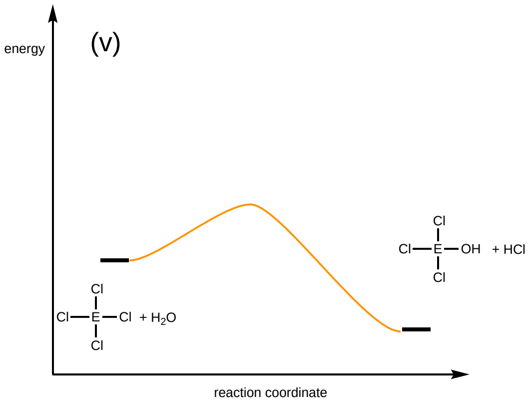
1-3. As described in Q1-2, it is important that silicon can adopt, in contrast to carbon, a penta-coordinate geometry in a meta-stable intermediate. This is due to the longer bond lengths of silicon relative to those of carbon; accordingly, there is a spatial margin around the central silicon atom, resulting in low repulsion between the five coordinated ligands. As can be found in Q1-2, although the bond-dissociation energy of each bond in the penta-coordinated silicon compound is smaller than that in the tetracoordinated silicon compound, the five weak bonds in the penta-coordinated silicon compounds should collectively yield sufficient stabilizing energy. Thus, the penta-coordinated silicon compound exhibits stability that is comparable to that of the corresponding tetracoordinated silicon compound. Based on the aforementioned considerations, **choose** the graphs that most appropriately represent the energy changes during the progress of reactions of (1) and (2), respectively.











Note that the vertical axes in figures (i)–(v) all have the same scale.

For certain elements A and B, the Pauling electronegativities χ_A and χ_B are defined according to the following equation:

$(\chi_A - \chi_B)^2 = D_{AB} - (D_{AA} + D_{BB}) / 2$

D_{AB}: Bond dissociation energy of an A–B bond [eV]
D_{AA}: Bond dissociation energy of an A–A bond [eV]
D_{BB}: Bond dissociation energy of a B–B bond [eV]

The Pauling electronegativities of hydrogen, nitrogen, and chlorine are as follows: $\chi_H = 2.10$, $\chi_N = 3.04$, $\chi_{Cl} = 3.16$. The bond-dissociation energies [kJ mol^{-1}] are as follows: N≡N: 945, O=O: 498, N–N: 158, H–H: 436, H–Cl: 426, Cl–O: 206, O–H: 467.

2-1. Based on these values, **calculate** the bond-dissociation energies D_{NH}, D_{NCl}, and D_{ClCl} for the N–H, N–Cl, and Cl–Cl bonds, respectively.

2-2. **Write** the molecular formulae that can apply to blanks **A** to **D** in the following sentence, and **calculate** the numerical value that applies to blank ***Q***.

The Pauling electronegativities of nitrogen and chlorine are $\chi_N = 3.04$ and $\chi_{Cl} = 3.16$, respectively, and thus, the polarity of the N–Cl bond can be considered to be N^+–Cl^-. For example, in the hydrolysis reaction of monochloroamine (H_2NCl), it would be expected that nitrogen-containing product **A** and chlorine-containing product **B** will be produced based on the N^+–Cl^- polarization. In the actual reaction, however, nitrogen-containing product **C** and chlorine-containing product **D** are produced, as shown in the equation below. This result cannot be interpreted in terms of the Pauling electronegativities. The reaction between monochloroamine and water can be written as follows, and the enthalpy change in this reaction can be calculated as $\Delta H = \boldsymbol{Q}$ [kJ] based on the values of the bond-dissociation energies, suggesting that this reaction should proceed endothermically.

$$\text{(eq.) } H_2NCl + H_2O \rightarrow \mathbf{C} + \mathbf{D} \qquad \Delta H = \boldsymbol{Q} \text{ [kJ]}$$

Allred and Rochow defined electronegativity using the equation below. The Allred–Rochow electronegativity (χ_{AR}) depends on the values of the effective nuclear charge for the valence electrons ($Z^{VE}{}_{eff}$) and the covalent radius of the atom (r [pm]), based on the idea that electronegativity should be determined by the strength of the electric field on the atomic surface.

$$\chi_{AR} = 3590\left(\frac{Z^{VE}{}_{eff} - 0.35}{r^2}\right) + 0.744$$

The effective nuclear charge (Z_{eff}) can be estimated according to Slater's rules as follows:

(i) Write the electron configuration for the atom using the following pattern, in which electrons in the s and p orbitals should be combined into the same group, while those in the d orbitals should be independent from those in the s and p orbitals. For example, [1s], [2s, 2p], [3s, 3p], [3d].
(ii) Identify the electron of interest and ignore all electrons in higher groups (larger "n" in [ns,np] group.). These do not shield electrons in lower groups.
(iii) Regarding the shielding experienced by an s- or p- electron, electrons within the same group contribute **0.35** to the shielding, except for 1s electrons, which contribute **0.30** to the shielding.
(iv) For the electrons in an [ns, np] group, the electrons in the n-1 group contribute **0.85** to the shielding.
(v) For the electrons in an [ns, np] group, electrons in the n-2 or lower groups contribute **1.00** to the

shielding.

(vi) For the electrons in an [nd] or [nf] group, electrons within same group contribute **0.35** to the shielding. All electrons in higher groups of [nd] and [nf] orbitals are ignored.

(vii) For the electrons in an [nd] or [nf] group, the electrons in the lower groups contribute **1.00** to the shielding.

For example, according to Slater's rule, in the case of silicon ($_{14}$Si), which exhibits an electron configuration of $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$, the effective nuclear charge for the valence electrons Z^{VE}_{eff} (Si) can be estimated as 4.15 [$= 14–(0.35\times3)–(0.85\times8)–(1.00\times2)$].

2-3. The covalent radii of nitrogen and chlorine are r(N) = 70.0 [pm] and r(Cl) = 99.0 [pm], respectively. Using the effective nuclear charge Z^{VE}_{eff} estimated with Slater's rules, **calculate** the Allred–Rochow electronegativities χ_{AR}(N) and χ_{AR}(Cl) of nitrogen and chlorine.

The electronegativity values based on the Allred–Rochow definition can explain the products in the hydrolysis reaction of monochloroamine. Thus, 'electronegativity' is a concept that was qualitative in nature and whose numerical values vary depending on the definition.

Problem 15. Sulfur in hot springs and volcanoes

Japan is known as a volcanic country, and the hot springs that are widely distributed throughout the country are deeply beloved. Hot springs exhibit different characteristics regarding *e.g.* temperature, acidity (pH), color, and smell, and are classified according to the chemical components they contain. Interestingly, many hot springs contain sulfur components.

1. Water from a certain hot spring (density: 1.00 g cm^{-3}) contains both thiosulfate ions and hydrogen sulfide. An excess of cadmium acetate is added to 100 mL of this hot spring water, and the resulting precipitate (9.50 mg) is separated by filtration. A small amount of starch is added as an indicator to the filtrate, and an aqueous I_2/KI solution (effective I_2 concentration: 2.50×10^{-2} mol L^{-1}) is slowly added dropwise. After the addition of 7.30 mL of the aqueous I_2/KI solution to the analyte, the coloration due to iodine came to appear. **Calculate** the total sulfur (S) content [mg kg^{-1}] in the initial hot spring water. Assume that sulfur is only derived from the thiosulfate ions and hydrogen sulfide and that no other species are involved in these reactions..

2. Hot springs that contain more than 2 mg of sulfur (S) derived from H_2S, HS^-, S^{2-}, and $S_2O_3^{2-}$ in 1.00 kg of hot spring water are known as 'sulfur springs'. In a water sample from a hot spring, the density is 1.00 g cm^{-3}, the pH is 8.000, $[S^{2-}]$ is 1.00×10^{-8} mol L^{-1}, and 5.26×10^{-5} mol of thiosulfate ion is present in 1.00 kg of the water. **Calculate** the total sulfur content [mg kg^{-1}] of this hot spring.
   The first and second acid dissociation constants of hydrogen sulfide are $K_1 = 9.50 \times 10^{-8}$ and $K_2 = 1.30 \times 10^{-14}$, respectively.

3. To investigate the content of hydrogen sulfide and sulfur dioxide contained in volcanic gas, 10.0 L of volcanic gas are sampled. The gas is absorbed into 500 mL of an aqueous I_2/KI basic solution (effective I_2 concentration: 2.00×10^{-2} mol L^{-1}) under basic conditions. The generated elemental sulfur is removed by filtration, and the volume of the filtrate is adjusted with water to give a total volume of 1.00 L. Two 100 mL aliquots of this solution are placed in two beakers, which are referred to as beakers **A** and **B**. Barium chloride is added to the solution in beaker **A** until no further precipitate appears, and 41.5 mg of white precipitate is isolated by filtration. The solution in beaker **B** is titrated with 2.00×10^{-2} mol L^{-1} sodium thiosulfate solution using starch as an indicator. After dropping 73.0 mL of the titrant into the solution, the coloration due to iodine disappears. **Calculate** the concentrations of hydrogen sulfide and sulfur dioxide in the volcanic gas [mol L^{-1}]. Assume that the only sulfur-containing components in this volcanic gas are hydrogen sulfide and sulfur dioxide, and that during the series of experiments described above, the hydrogen sulfide does not react with the sulfur dioxide directly, since they are present under dilute conditions. Additionally, assume that the only substances that react during this series of experiments are hydrogen sulfide, sulfur dioxide, and the related substances generated from them.

Problem 16. Identification of unknown compounds and allotropes

Part 1. Identification of inorganic compounds

$\boxed{\text{A}}$ is a crystalline solid of a binary compound. It contains a metal ion X^{n+} and is grayish-white in color. $\boxed{\text{A}}$ slowly reacts with water at room temperature to form $\boxed{\text{B}}$, which is scarcely soluble in water; the generation of a gas is observed during this reaction. Dehydration reaction occurs upon heating $\boxed{\text{B}}$ at approximately 350 °C to form the white compound $\boxed{\text{C}}$, which contains 39.7 weight% of oxygen atoms. Heating $\boxed{\text{A}}$ generates gas of an amount of 7.6 weight% based on $\boxed{\text{A}}$, and the elemental metal X is formed. (i) Heating a mass *M* [g] of X under an N_2 atmosphere provides a yellow-green metal nitride. (ii) This metal nitride reacts with a large amount of water to generate $\boxed{\text{D}}$. The amount of $\boxed{\text{D}}$ corresponds to the gas of volume 120 mL at 1 bar and 25 °C.

1-1. **Write** the chemical formulae of compounds $\boxed{\text{A}}$, $\boxed{\text{B}}$, $\boxed{\text{C}}$, and $\boxed{\text{D}}$.

1-2. **Write** the chemical reactions corresponding to the underlined parts (i) and (ii).

1-3. **Calculate** the weight *M* [g].

Part 2. Allotropes

The term "allotrope" refers to one or more physical forms of a chemical element that occur in the same physical state. Allotropes generally exhibit different physical properties and may also differ in their chemical reactivity. For example, graphite and diamond have long been known as allotropes of carbon, and more recently, fullerenes and carbon nanotubes have been discovered as further carbon allotropes. One of the allotropes of phosphorus is a solid composed of P_4 molecules, which is called white phosphorus. It has a low melting point of 44 °C and is highly toxic, so care must be taken in its storage.

2-1. The solution ^{13}C NMR spectrum of fullerene C_{60} (Figure 1) exhibits $\boxed{\text{E}}$ peak(s). X-ray diffraction measurements have revealed $\boxed{\text{F}}$ different covalent carbon–carbon bond length(s) in the crystal structure of fullerene C_{60}. **Write** the appropriate integer values for $\boxed{\text{E}}$ and $\boxed{\text{F}}$.

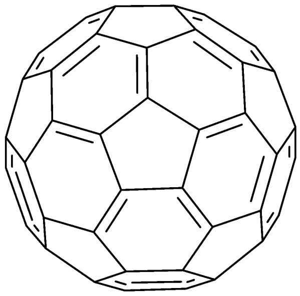


Figure 1. Structure of fullerene C_{60}.

2-2. Fullerene C_{60} forms a crystal via van der Waals forces. The crystal structure of fullerene C_{60} at room temperature is composed of a cubic unit cell with dimensions of 1.41 nm on each side. The molecules are located at all vertices and at the centers of all faces of the cubic unit cell. **Calculate** the density [g cm^{-3}] of the crystal of fullerene C_{60}.

2-3. The P_4 molecule has high structural symmetry, and all the P–P–P bond angles are 60°. **Draw** the steric structure of P_4.

Dioxygen and ozone are the allotropes of oxygen. Ozone acts as a strong oxidizing agent. For example, (iii) the oxidation reaction of potassium iodide by ozone in aqueous solution is accompanied with the generation of dioxygen, and the reaction is used for the quantitative determination of ozone. Ozone also exists in the stratosphere and acts as a filter that absorbs harmful ultraviolet light from sunlight. Dioxygen in the stratosphere is irradiated with ultraviolet light of wavelengths < 240 nm, where a dioxygen molecule is split into two oxygen atoms that react with another dioxygen molecule to produce ozone. On the other hand, ozone decomposes into dioxygen molecule and an oxygen atom when exposed to ultraviolet light with a wavelength of 240–315 nm. When these formation and decomposition reactions of ozone are in equilibrium, the concentration of ozone in the stratosphere is maintained at a constant level, blocking short-wave ultraviolet rays that are harmful to humans on the ground. In contrast, (iv) atmospheric nitric oxide reacts with ozone, and (v) nitrogen dioxide reacts with oxygen atoms, resulting in (vi) a reaction that converts ozone into dioxygen. This creates an ozone hole that can allow harmful ultraviolet radiation from the sun to reach the surface on the earth.

2-4. **Write** the reaction formula for the underlined part (iii).

2-5. *N* [mol] of ozone is bubbled through 15 mL of an aqueous solution of potassium iodide with a concentration of 1.0 mol L^{-1}; we assume that the ozone reacts completely. The solution is then titrated with an aqueous solution of sodium thiosulfate with a concentration of 0.20 mol L^{-1}; the titration requires 3.5 mL of the sodium thiosulfate solution. **Calculate** *N* [mol].

2-6. **Write** the reaction formulae for the underlined parts (iv)–(vi).

Problem 17. Metal oxides

1. In the crystal structures of most metal oxides, the oxide ions (O^{2-}) form a close-packed structure, wherein the metal ions occupy the voids created by O^{2-}. Figure 1(a) shows the cubic close-packed structure created by O^{2-}. Note that the ionic radius of O^{2-} is 0.140 nm. Answer the following questions.

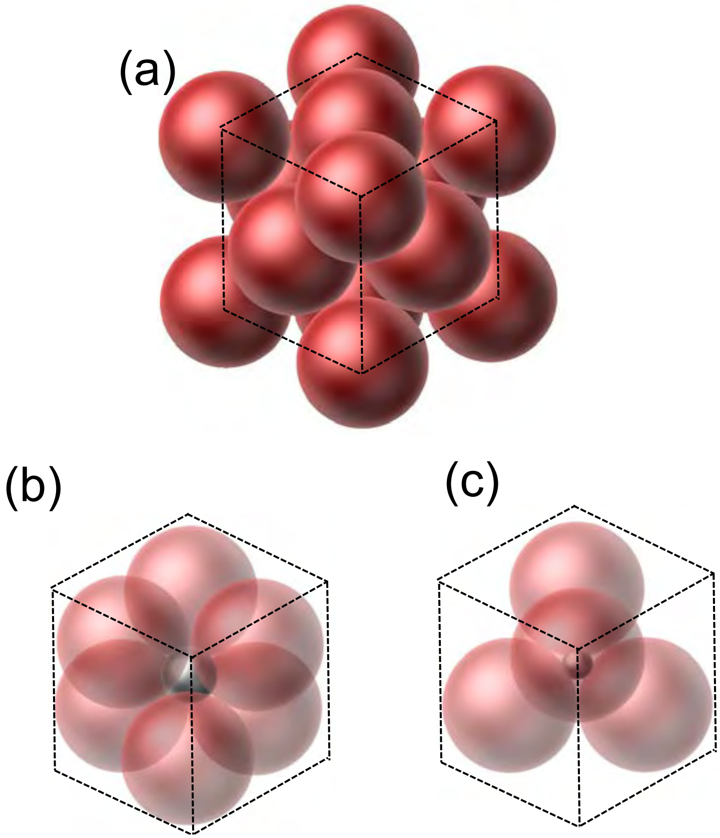


Figure 1. (a) Cubic close-packed structure formed by O^{2-} in metal oxides, (b) octahedral void, (c) tetrahedral void. ● O^{2-} ions, ● voids.

1-1. Considering O^{2-} as solid spheres in contact with each other, **calculate** the percentage volume of the voids in a cubic close-packed structure.

1-2. With reference to Figure 1(b) and (c), **calculate** the maximum radii of the spheres that can be placed in the octahedral and tetrahedral voids of a cubic close-packed structure composed of O^{2-}, respectively.

1-3. **Write** the chemical formula for a ternary metal oxide $A_xB_yO_z$ wherein one metal ion (A) occupies 1/8 of the tetrahedral voids in a cubic close-packed structure composed of O^{2-}, and a second metal ion (B) occupies 1/2 of the octahedral voids.

1-4. Regular arrays of atoms, ions, or molecules in solids are represented by a repeating unit known as the unit cell. In $SrTiO_3$, which adopts a perovskite structure, the ionic radii of Sr^{2+} and O^{2-} are comparable, and a cubic close-packed structure is formed by Sr^{2+} and O^{2-}. The Ti^{4+} ions occupy all octahedral voids formed by O^{2-}. Based on this information, **draw** the unit cell of $SrTiO_3$ with reference to Figure 2, assuming Ti^{4+} (●) is located at the center of the cube. Draw Sr^{2+} as ● and O^{2-} as ×.

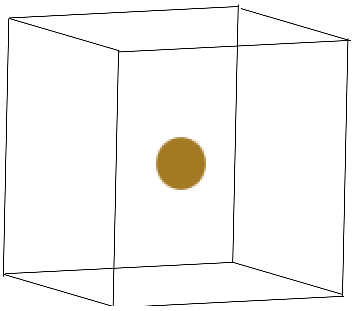


Figure 2. Unit cell of $SrTiO_3$ showing only Ti^{4+} at the center.

Most divalent metal oxides (MO) crystallize in a rock salt structure wherein M^{2+} occupies the octahedral voids created by O^{2-} (Figure 3).

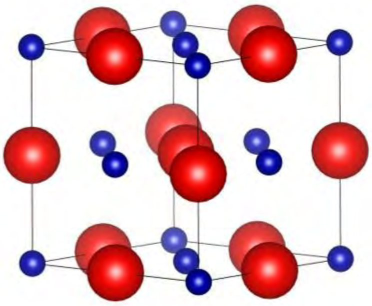


Figure 3. Unit cell of CaO. Blue and red spheres represent Ca^{2+} and O^{2-}, respectively. (● Ca^{2+}, ● O^{2-})

The thermodynamic properties of metal oxides can be discussed in terms of the standard molar enthalpy change (ΔH_{Lexp}) associated with the formation of gaseous ions from the ionic solid:

$$MO(s) \rightarrow M^{2+}(g) + O^{2-}(g) \quad \Delta H_{\text{Lexp}} \qquad (1)$$

ΔH_{Lexp} is known as the lattice enthalpy; although it cannot be measured directly, it can be determined from enthalpy data (Table 1) using a Born–Haber cycle, which is a closed path of steps that includes lattice formation as one stage.

Table 1. Enthalpy changes of reactions involved in the Born–Haber cycle

Steps	Enthalpy change [kJ mol^{-1}]
Sublimation of Ca(s): $Ca(s) \rightarrow Ca(g)$	+193
Ionization of Ca(g) to $Ca^{+}(g)$: $Ca(g) \rightarrow Ca^{+}(g) + e^{-}(g)$	+590
Ionization of $Ca^{+}(g)$ to $Ca^{2+}(g)$: $Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^{-}(g)$	+1010
Dissociation of O_2: $O_2(g) \rightarrow 2\ O(g)$	+498
Electron gain by O(g): $O(g) + e^{-}(g) \rightarrow O^{-}(g)$	–141
Electron gain by $O^{-}(g)$: $O^{-}(g) + e^{-}(g) \rightarrow O^{2-}(g)$	+878
Formation of CaO(s): $Ca(s) + \frac{1}{2} O_2(g) \rightarrow CaO(s)$	–635

2-1. **Calculate** the ΔH_{Lexp} [kJ mol^{-1}] of CaO using the enthalpy data in Table 1 and the Born–Haber cycle.

The lattice enthalpy of an ionic crystal can be calculated theoretically ($\Delta H_{\mathrm{Lcalc}}$) from the sum of the Coulomb energies between the constituent ions as point charges. The Coulomb energy E between ions is expressed by the following equation:

$$E = \frac{1}{4\pi\varepsilon_0}\frac{Z_1 Z_2 e^2}{r} \qquad (2)$$

where ε_0 is the permittivity of the vacuum, e the elementary charge, Z_1 and Z_2 the charge numbers of the ions, and r the distance between the ions. E is attractive (*i.e.*, negative) between an anion and a cation, while E is repulsive (*i.e.*, positive) between two anions or two cations.
Ca^{2+} is surrounded by six O^{2-} in an octahedral arrangement (Figure 4).

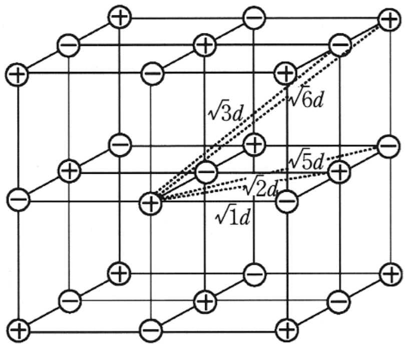


Figure 4. A unit cell of a rock salt structure to calculate the Madelung constant.

For a distance d between Ca^{2+} and O^{2-} in the rock salt structure depicted in Figure 4, the Coulomb energy (E_1) between a Ca^{2+} and six O^{2-} is formulated as follows:

(3)

In the structure depicted in Figure 4, twelve Ca^{2+} are located at a distance of $\sqrt{2}d$ from a given Ca^{2+}. The Coulomb energy (E_2) between the Ca^{2+} and the twelve surrounding Ca^{2+} is formulated as follows:

(4)

Similarly, for any given Ca^{2+}, there are 8 O^{2-}, 6 Ca^{2+}, 24 O^{2-}, and 24 Ca^{2+} at distances of $\sqrt{3}d$, $\sqrt{4}d$, $\sqrt{5}d$, and $\sqrt{6}d$, respectively. The overall Coulomb energy E_{all}, obtained by the summation of E_{n} converges to the following equation:

$$E_{\mathrm{all}} = \frac{N_{\mathrm{A}} Z^{+} Z^{-} e^2}{4\pi\varepsilon_0 d} M \qquad (5)$$

where Z^{+} and Z^{-} are the charge numbers of the cation and anion, respectively; N_{A} is Avogadro's constant, and M is the Madelung constant, which is 1.748 for the rock salt structure. The theoretical lattice enthalpy $\Delta H_{\mathrm{Lcalc}}$ is calculated using the Born–Mayer equation below, which takes into account the electron–electron and nucleus–nucleus repulsion of nearby ions:

$$\Delta H_{\mathrm{Lcalc}} = \frac{N_{\mathrm{A}}|Z^{+}Z^{-}|e^{2}}{4\pi\varepsilon_{0}d}\left(1 - \frac{d^{*}}{d}\right)M \qquad (6)$$

where d^* is a constant (typically: 0.0345 nm).

2-2. **Fill in** the blanks (3) and (4) with the appropriate equations.

2-3. **Calculate** $\Delta H_{\mathrm{Lcalc}}$ [kJ mol^{-1}] for CaO using equation (6); use $d = 0.240$ nm.

Problem 18. Coordination chemistry and its application to solid-state catalysts

Transition-metal complexes are formed by the coordination of ligands (*e.g.*, H_2O and NH_3) to transition metals or their ions. Most transition-metal complexes exhibit beautiful colors that cannot be explained by the classical theory of chemical bonding. Therefore, crystal-field theory has been developed; the repulsion between the d-electrons and the lone pairs of the ligands as negative point charges splits the energy of the five degenerate d-orbitals. Transition-metal complexes exhibit color because this energy separation and the corresponding transitions coincide with the energy of visible light.

Consider an octahedral transition-metal complex with the metal ion at the origin of a three-dimensional coordinate system and a total of six ligands as negative point charges equidistant from the origin on the *x*, *y*, and *z* axes (Figure 1a). The energies of the five degenerate d-orbitals are split into two groups called the e_g and t_{2g} orbitals, which are oriented along and between the axes, respectively.

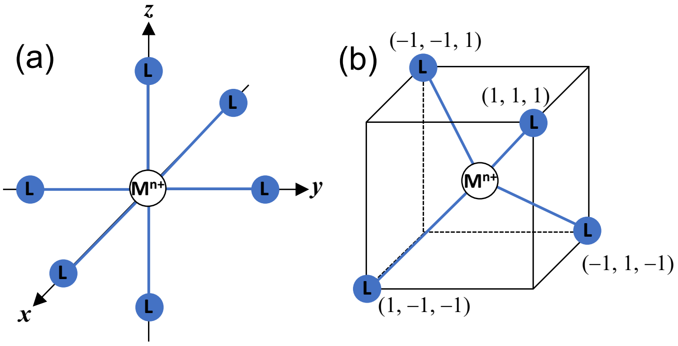


Figure 1. Arrangement of the metal ion (M^{n+}) and ligands (L) in (a) octahedral and (b) tetrahedral complexes. Blue solid lines represent the coordination bonds. The metal ion is located at the origin (0, 0, 0) of the three-dimensional coordinate system. The coordinates of the four ligands in the tetrahedral complex are indicated for clarity.

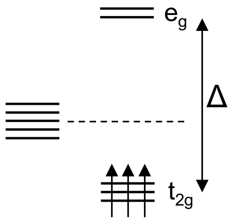
1. **Classify** the five d-orbitals into e_g and t_{2g} orbitals.

Let the energy separation between the e_g and t_{2g} orbitals (*i.e.*, the crystal-field splitting parameter) be Δ_O, where the subscript O signifies an octahedral arrangement. The barycenter of the energies of the e_g and t_{2g} orbitals is equal to the energy of the five degenerate d-orbitals.

2. **Write** the energies of the e_g and t_{2g} orbitals relative to the barycenter in units of Δ_O.

The energetically split d-orbitals, caused by the repulsion between the transition metal ion and the ligands, accommodate electrons according to Hund's rule. For example, Ti^{3+} with one d-electron (d^1) forms an octahedral complex $[Ti(H_2O)_6]^{3+}$; this complex is energetically more stable than Ti^{3+} without ligands. This additional stability relative to the barycenter is known as the 'crystal field stabilization energy' (CFSE). The first through third d-electrons (d^1 to d^3) are exclusively accommodated in the t_{2g} orbitals. However, there are two possible ground-state electron configurations for d^4 to d^7. Namely, Hund's rule applies when the CFSE is small, resulting in a 'high-spin' ground state with a large number of unpaired electrons. On the other hand, Hund's rule does not apply when the CFSE is large, resulting in a 'low-spin' ground state with a smaller number of unpaired electrons. In general, the CFSE depends on the type of ligands (*cf.* spectrochemical series).

3. **Draw** the high-spin electron configurations of octahedral complexes for d^4-d^7 by referring to the electron configuration of d^3 shown below, and **calculate** each CFSE in units of Δ_O.



While six-coordinate octahedral complexes are the most common among the transition-metal complexes, four-coordinate complexes are also very frequently encountered. There are two types of four-coordinate complexes, tetrahedral and square planar complexes. Of these two, tetrahedral complexes have a lower steric repulsion between the ligands, and similarly to octahedral complexes, the energy splitting of their d-orbitals can be considered using crystal-field theory. In the tetrahedral crystal field (Figure 1b), the energy of the five degenerate d-orbitals is split into two sets of orbitals, e and t_2 orbitals.

4. **Draw** the energy separation between the e and t_2 orbitals with Δ_T as the crystal-field splitting parameter, where the subscript T signifies a tetrahedral arrangement. **Classify** the five d-orbitals into e and t_2 orbitals. **Write** the energies of e and t_2 orbitals relative to the barycenter in units of Δ_T.

When an aqueous solution containing the octahedral complex $[Ti(H_2O)_6]^{3+}$ is irradiated with visible light, a d-electron is excited from the t_{2g} to the e_g orbital, which is accompanied by the absorption of green light ($\lambda = 500$ nm). Consequently, the aqueous solution takes on a red-purple color, which is the complementary color of green.

5. **Calculate** the energy separation Δ_O (kJ mol^{-1}) between the e_g and t_{2g} orbitals in $[Ti(H_2O)_6]^{3+}$.

Transition-metal complexes with carbon monoxide (CO) as a ligand are called metal carbonyls. Representative examples are the octahedral $Cr(CO)_6$ and tetrahedral $Ni(CO)_4$ complexes. The total number of electrons provided by the metal and ligands in a transition-metal complex is called the effective atomic number (EAN), and the 18-electron rule states that a complex is stable when the EAN is equal to the atomic number of noble gases. For instance, Cr and the CO ligands in $Cr(CO)_6$ supply 6 and $2 \times 6 = 12$ electrons, respectively; similarly, Ni and the CO ligands in $Ni(CO)_4$ supply 10 and $2 \times 4 = 8$ electrons, respectively, satisfying the 18-electron rule for each metal carbonyl. In addition to mononuclear metal carbonyls with one metal atom, there are also multinuclear metal carbonyls with multiple metal atoms and metal–metal bonds.

6. **Draw** the molecular structure of $Mn_2(CO)_{10}$ and $Ir_4(CO)_{12}$ and show that the EAN per metal atom is 18.

The coordination bonds formed between carbon monoxide (CO) and metals can be used to estimate the size of metal nanoparticles loaded on catalyst support such as Al_2O_3. Figure 2a shows a schematic illustration of a platinum catalyst supported on alumina (Pt/Al_2O_3), which is used as an automotive catalyst.

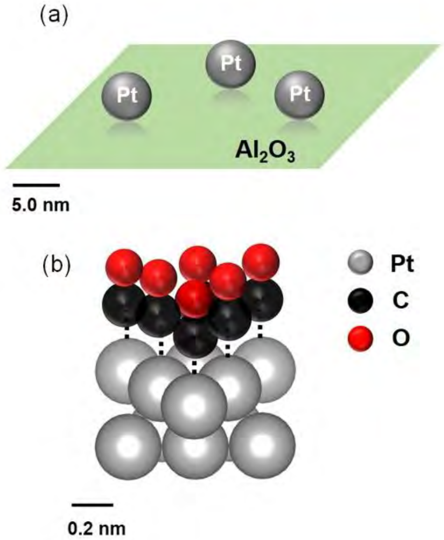


Figure 2. Schematic illustrations of (a) the Pt/Al_2O_3 catalyst and (b) the CO molecules adsorbed on the Pt surface. The Pt metal particles in (a) are the same size.

1.0 g of Pt/Al_2O_3 catalyst that contains 0.010 g of Pt metal is prepared. Upon exposure to CO gas, 0.55 mL (1.0 bar, 273 K) of CO was adsorbed per 1.0 g of catalyst. The Pt metal particles on Al_2O_3 are spherical, and their surfaces can be regarded as being covered with Pt atoms without gaps. As shown in Figure 2b, one CO molecule coordinates to one Pt atom exposed on the surface. The density of the Pt metal is 21.45 g cm^{-3}, and the area occupied by each Pt atom is 8.0×10^{-2} nm^2.

7. Answer the following questions.

7-1. **Calculate** the ratio [%] of Pt atoms exposed on the surface to the total number of Pt atoms in the spherical Pt metal particles.

7-2. **Calculate** the number of CO molecules adsorbed per 1.0 g of Pt metal dispersed on the Al_2O_3 support.

7-3. **Calculate** the surface area [m^2] per 1.0 g of Pt metal.

7-4. **Calculate** the diameter of the Pt metal particles.

Problem 19. Acids and bases

In 1923, Brønsted and Lowry defined an acid–base reaction as the transfer of a proton (H^+) from the proton donor (acid) to the proton acceptor (base).

$$HF + H_2O \rightleftharpoons H_3O^+ + F^- \qquad (1)$$
$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^- \qquad (2)$$

Hydrogen fluoride (HF) is an example of a Brønsted acid, ammonia (NH_3) is an example of a Brønsted base, while water (H_2O) is amphoteric, *i.e.*, it can behave as both a Brønsted acid and a Brønsted base. When acid–base reactions are in chemical equilibrium, the reactions are indicated by two one-sided arrows as in (1) and (2). When HF donates a proton to H_2O, F^- and H_3O^+ are formed as the conjugate base and conjugate acid, respectively. Brønsted acidity can be evaluated quantitatively using the acidity constant, or qualitatively using the (a) stability of the conjugated base.

1. **Arrange** the following Brønsted acids in order of increasing acidity by referring to the underlined part (a).

$$HClO \quad HClO_2 \quad HClO_3 \quad HClO_4$$

The Brønsted acidity of hydrogen halides (HX, X = F, Cl, Br, I) can be evaluated by the standard enthalpy change (ΔH°_{HX}) of the protonation reaction of their conjugate bases (X^-):

$$X^-(g) + H^+(g) \rightarrow HX(g) \qquad \Delta H^\circ_{HX} \quad (3)$$

This reaction can be divided into three steps:

Electron loss from X^-: $X^-(g) \rightarrow X(g) + e^-(g)$ $\quad \Delta H^\circ_1$ (4)
Electron gain by H^+: $H^+(g) + e^-(g) \rightarrow H(g)$ $\quad \Delta H^\circ_2$ (5)
Combination of H and X: $H(g) + X(g) \rightarrow HX(g)$ $\quad \Delta H^\circ_3$ (6)

Therefore, ΔH°_{HX} is calculated as $\Delta H^\circ_{HX} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3$.

2. **Calculate** the absolute value of ΔH°_{HF} ($|\Delta H^\circ_{HF}|$ in kJ mol^{-1}) by drawing a thermodynamic cycle for the protonation reaction of F^-. Use the following values if necessary:
   H–F bond dissociation enthalpy: 567 kJ mol^{-1}; ionization enthalpy of hydrogen: 1312 kJ mol^{-1}; enthalpy of electron gain by fluorine: –328 kJ mol^{-1}.

3. **Calculate** the absolute value of ΔH°_{HI} ($|\Delta H^\circ_{HI}|$ in kJ mol^{-1}) by drawing a thermodynamic cycle for the protonation reaction of I^-. Use the following values if necessary:
   H–I bond dissociation enthalpy: 298 kJ mol^{-1}; enthalpy of electron gain by iodine: –295 kJ mol^{-1}.

4. According to Q2 and Q3, $|\Delta H^\circ_{HI}|$ (a)_ $|\Delta H^\circ_{HF}|$; therefore, the Brønsted acidity of hydrogen halides is arranged in the following order, HF (b)_ HCl (b)_ HBr (b)_ HI. **Choose** which inequality sign, '>' or '<', should be placed in blanks a and b.

Metal ions are hydrated in aqueous solutions, and generally, the first hydration shell of metal ions consists of six water molecules. When the oxygen atom of a water molecule is strongly coordinated to a metal ion, the coordinated water acts as a proton donor as shown in (7).

$$[M(OH_2)_6]^{n+}(aq) + H_2O(l) \rightleftharpoons [M(OH_2)_5(OH)]^{(n-1)+}(aq) + H_3O^+(aq) \quad (7)$$

5. **Arrange** the following aqua acids in order of increasing acidity.

$$[Na(H_2O)_6]^+ \quad [Ca(H_2O)_6]^{2+} \quad [Fe(H_2O)_6]^{3+} \quad [Zn(H_2O)_6]^{2+}$$

Lewis introduced a more general concept of acids and bases, which includes reactions that do not involve protons. Lewis defined an acid–base reaction as the transfer of an electron pair from the electron-pair donor (Lewis base) to the electron-pair acceptor (Lewis acid). Note that the Brønsted acid HA is a complex formed by the Lewis acid H^+ with the Lewis base A^-. All Brønsted acids and Brønsted bases exhibit Lewis acidity and Lewis basicity, respectively.

6. **Identify** the Lewis acids and bases in each of the following reactions.

   (i) $BF_3 + NH_3 \rightarrow BF_3NH_3$
   (ii) $Ni + 4\ CO \rightarrow [Ni(CO)_4]$
   (iii) $CO_2 + OH^- \rightarrow HCO_3^-$
   (iv) $SiF_4 + 2\ F^- \rightarrow SiF_6^{2-}$

7. Phosphoric acid (H_3PO_4) and boric acid (H_3BO_3) are both acids with three hydrogens. While phosphoric acid reacts as a triprotic Brønsted acid, boric acid reacts as a monoprotic acid. **Draw** the Lewis structure of the conjugate base of boric acid by considering the reaction with water.

Problem 20. Semiconductors

In molecules that exist as gases or liquids, the molecular orbitals are formed by the overlap between the atomic orbitals of individual atoms. In contrast, in the electronic state of a solid composed of an infinite number of atoms, many atomic orbitals are overlapping; therefore, many molecular orbitals with close energy levels are formed. As the gap between their energy levels is very narrow, these orbitals are for practical reasons represented as an energy band. Insulators have a wide energy gap between the valence band (VB), which is completely filled with electrons, and the conduction band (CB), which does not contain electrons (Figure 1).

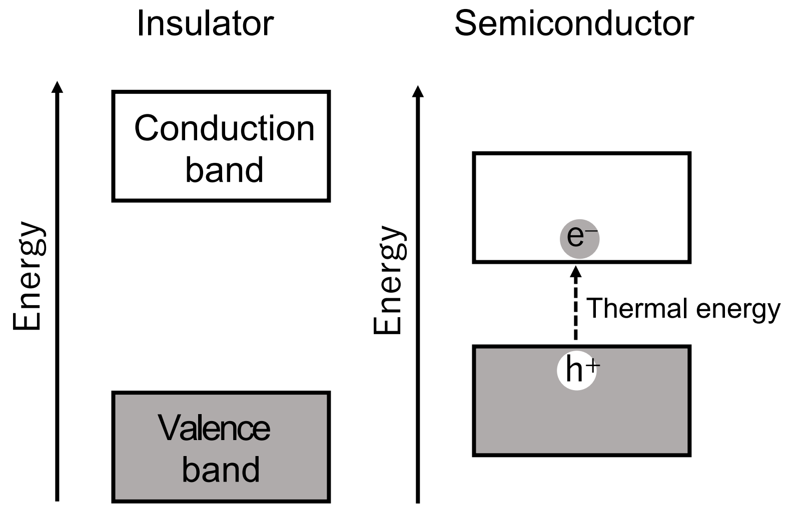


Figure 1. Schematic view of the electronic band structure in solid-state materials.

In insulators, the electrons are bound within the VB. On the other hand, in semiconductors, some electrons (e^-) in the VB can be transferred to the CB by thermal energy, as the energy gap between the VB and CB is relatively small. An electron transition in a semiconductor creates a hole in the VB; this hole behaves like a positively charged particle. The hole is commonly referred to as h^+. The electrons and holes formed in the semiconductor can move, which results in electrical conductivity.

1. With reference to Figure 1, **illustrate** the band structure of a metallic conductor, which shows electrical conductivity even when the temperature is lowered.

Semiconductors are classified as either intrinsic or extrinsic semiconductors. An intrinsic semiconductor is composed of a pure material, and the same number of electrons and holes are produced by thermal energy and other factors. The electrical conductivity is not very high. On the other hand, there are two types of extrinsic semiconductors, n-type and p-type, whose electrical conductivity is generally higher than that of intrinsic semiconductors. In n-type semiconductors, small amounts of electrons are added to a pure material (electron doping), while in p-type semiconductors, small amounts of holes are added to a pure material (hole doping). For example, adding a small amount of P to pure Si, a typical intrinsic semiconductor, results in the doping of an extra electron (Figure 2). Accordingly, P-doped Si exhibits n-type semiconductor properties.

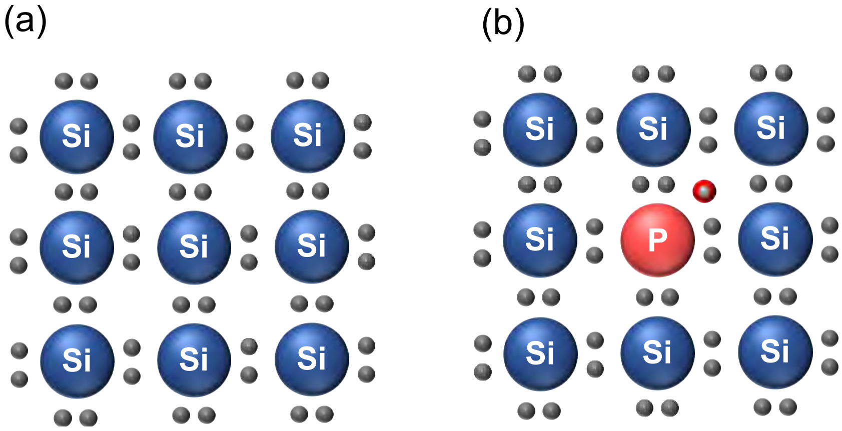


Figure 2. Schematic view for electron states of (a) Si and (b) P-doped Si.

2. **Indicate** which elements in the following list could be used to produce p-type semiconductor properties in Si.

Ga, Ge, As, B

TiO_2, a representative oxide semiconductor, is capable of inducing the water-splitting reaction at room temperature using light energy as a driving force. The water-splitting reaction, which generates hydrogen (H_2) from water, is expected to be a significant source of renewable energy in the near future. The discovery of the following phenomena is one reason for the development of photocatalysts such as TiO_2. (1) The electrolysis of water occurs when a voltage is applied. In contrast, (2) when TiO_2 and platinum electrodes are arranged as shown in Figure 3 and the TiO_2 side is exposed to light irradiation, oxygen and hydrogen are generated from each electrode. This phenomenon is called the Honda–Fujishima effect and was discovered in 1972. Electrons and holes are produced by irradiating TiO_2 with light, which leads to the reduction and oxidation of water, respectively.

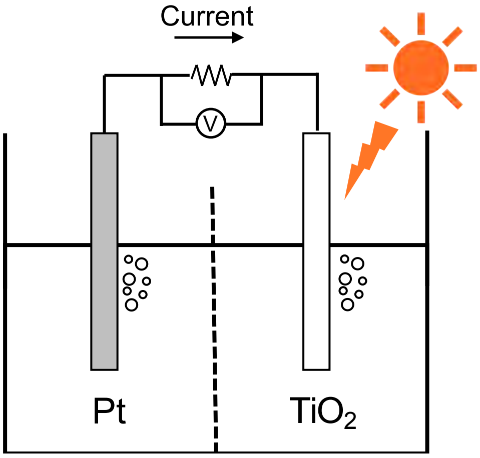


Figure 3. Schematic illustration of the photoelectrochemical water-splitting reaction.

3-1. When TiO_2 is subjected to a thermal treatment under an H_2 flow, it exhibits n-type semiconductor properties. **Explain** the reasons for this phenomenon.

3-2. Regarding the underlined part in (1), **calculate** the voltage at which water can be thermodynamically electrolyzed. The standard Gibbs energy change for the splitting of 1 mole of water is 237 kJ.

3-3. **Write** the half-reaction equation including the hole (h^+) for the gas-evolution reaction on TiO_2 described in the underlined part in (2). When TiO_2 is exposed to light irradiation, a current is observed in the direction shown in Figure 3.

3-4. **Choose** the option below that best represents the maximum percentage of the photon number in sunlight that is available for water-splitting reactions on TiO_2. The band gap of TiO_2 between the VB maximum and the CB minimum is 3.0 eV. Figure 4 shows the solar spectrum, and the calculation of the photon number here does not take into account sunlight below 300 nm and above 800 nm.

(a) <1.0 % (b) 1–10 % (c) 10–20 % (d) 20–30 %

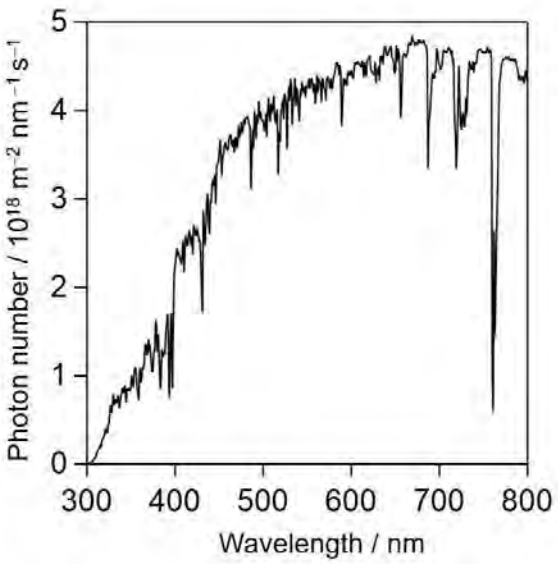
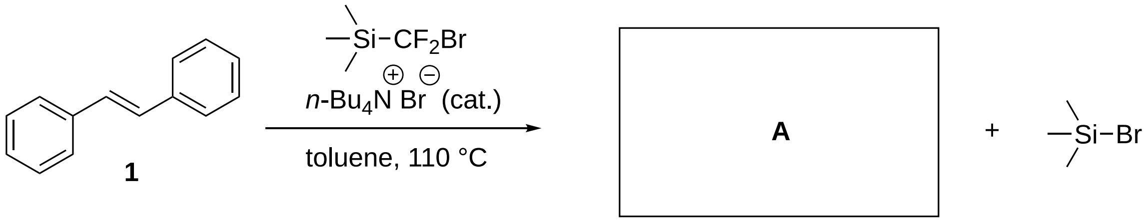


Figure 4. Photon number vs wavelength in sunlight.

3-5. The ratio of the number of carriers (electrons or holes) consumed in the water-splitting reaction to the number of irradiated photons is called quantum efficiency. When TiO_2 is irradiated with 1.00 W of light with a wavelength of 350 nm, 5.00 μmol of hydrogen are produced in 100 seconds. **Calculate** the quantum efficiency [%].

Problem 21. Carbenes and non-benzenoid aromatic compounds

The following problems describe the highly unusual and interesting reactivity of carbenes.



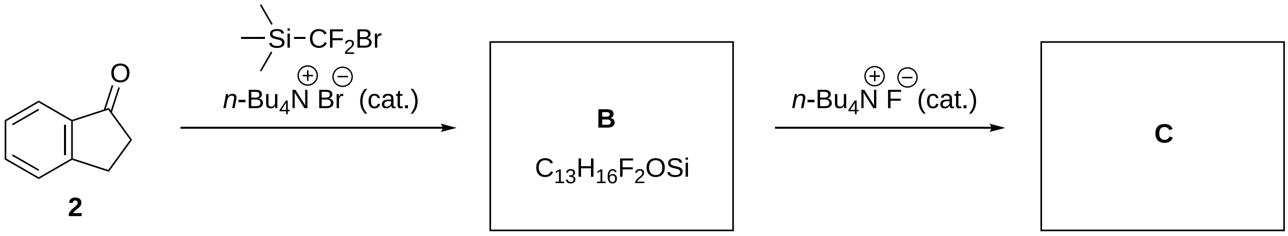
^{1}H NMR 7.23 ppm (10H), 2.95 ppm (2H)

^{19}F NMR –134.5 ppm (triplet, *J* = 8.5 Hz)

Under the conditions described above, olefin **1** is converted into **A**, which does not contain a double bond.

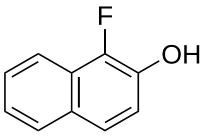
1. **Draw** the structure of **A**.

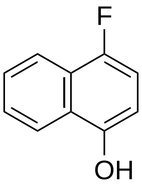
Under similar reaction conditions, tautomer of ketone **2** is converted into **B**, which is subsequently transformed into **C** in the presence of a fluoride ion.

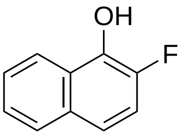


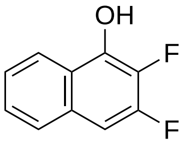
2. **Draw** the structure of **B**.

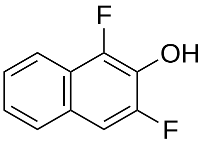
3. **Choose** all possible structures for **C**.

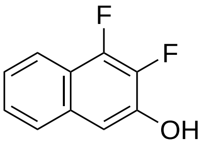
a


b


c


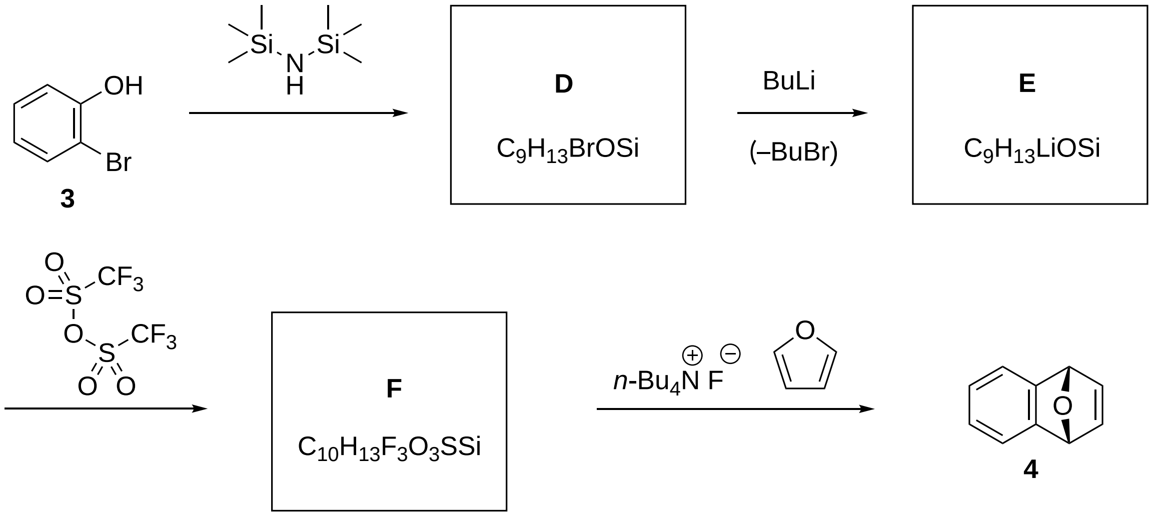
d


e


f


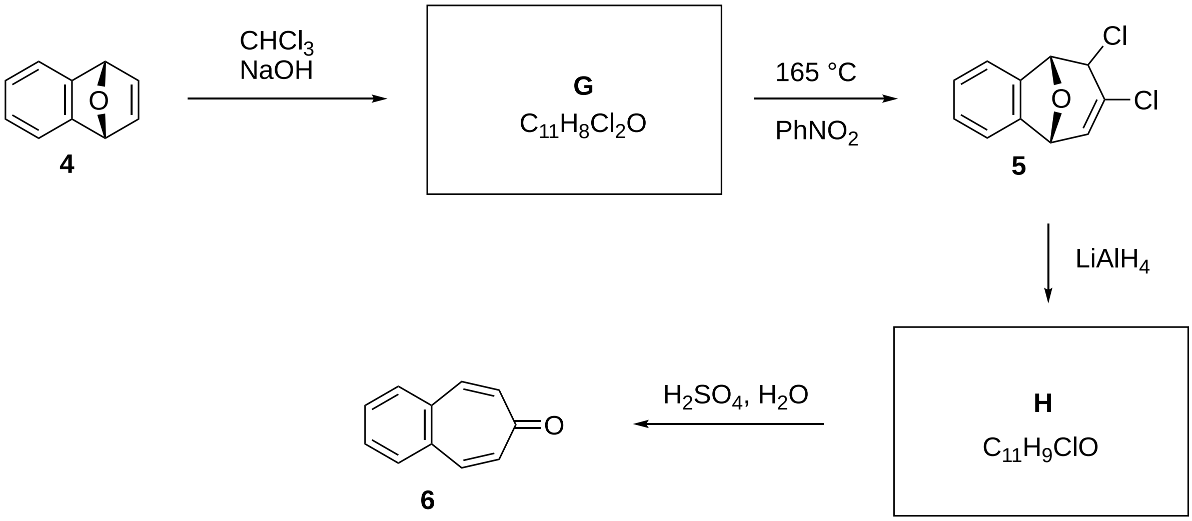
Silicon exhibits an extremely high affinity toward oxygen and especially fluorine. An application that capitalizes on this reactivity is the formation of benzyne species.

4. A four-step transformation converts **3** into **4**. **Draw** the structures of **D**–**F**.



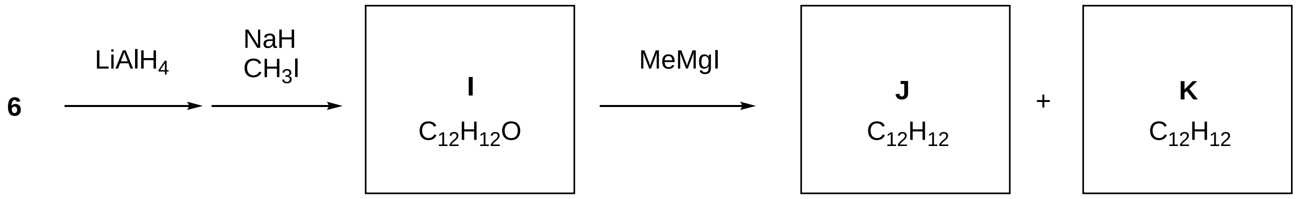
In another four steps, **4** is converted into **6**, which bears a cycloheptatrienone moiety. The structure of **G** contains one more cyclic moiety than the structure of **4**.

5. **Draw** the structure of **G** (while the stereochemistry is important for the reaction, it is not the focus of this question).



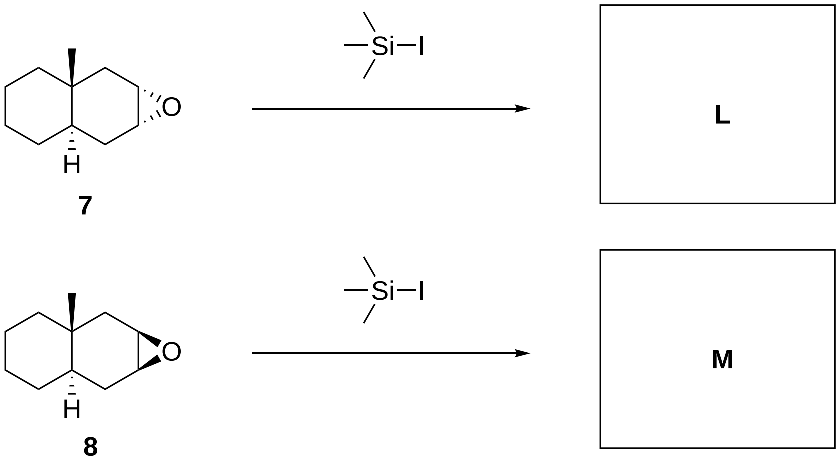
6. **Draw** the structure of **H**.

Subsequently, **6** is converted into **I** by exploiting the unique aromaticity of cycloheptatriene cations. When **I** is treated with the Grignard reagent MeMgI, a mixture of **J** and **K** is obtained. Treating **I** with catalytic amount of HCl in CCl_4 furnishes isomer **I’**, which is again converted into a mixture of **J** and **K** upon treatment with Lewis-acidic Grignard reagents.



7. **Draw** the structures of **I**, **J**, **K**.

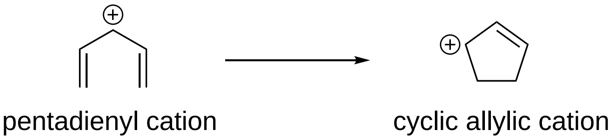
The ring-opening of the epoxide moiety on the six-membered ring occurs so that both the introduced functional group and the hydroxy leaving group adopt axial positions. Epoxides **7** and **8** both react with trimethylsilyl iodide, but afford different products.



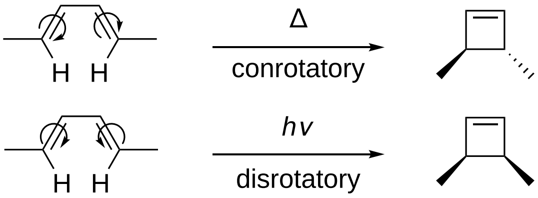
8. **Draw** the structures of **L** and **M**.

Problem 22. Nazarov cyclization

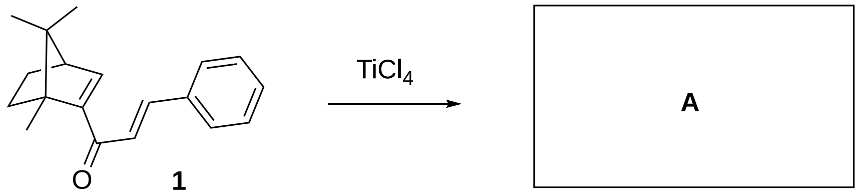
The formation of five-membered rings is a very important class of organic transformations. Answer the following questions regarding one of those interesting reactions, the so-called ‘Nazarov cyclization’.



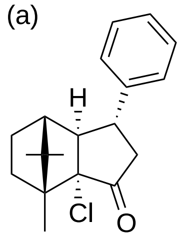
In general, 4π-electrocyclization reactions proceed via one of two cyclization modes. Conrotatory cyclization occurs under thermal transformation conditions, while disrotatory cyclization occurs upon photoirradiating the substrate.



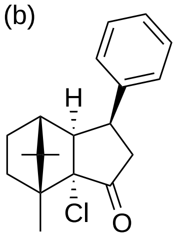
1. Titanium tetrachloride ($TiCl_4$) is a Lewis acid that can activate the carbonyl group in **1**. The resulting pentadienyl cation intermediate is transformed via a conrotatory Nazarov cyclization. The resulting cation intermediate is then trapped with chloride to give **A**. **Choose** all possible structures of **A**.



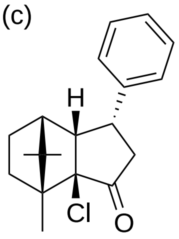
(a)



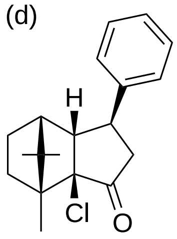
(b)



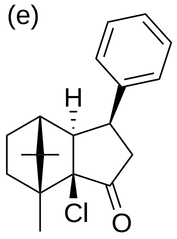
(c)



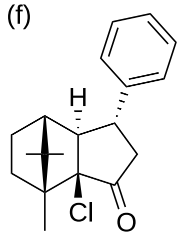
(d)



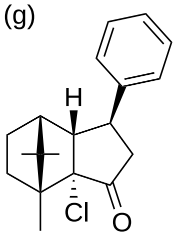
(e)



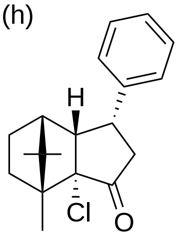
(f)



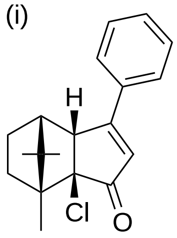
(g)



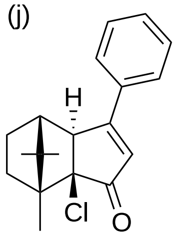
(h)



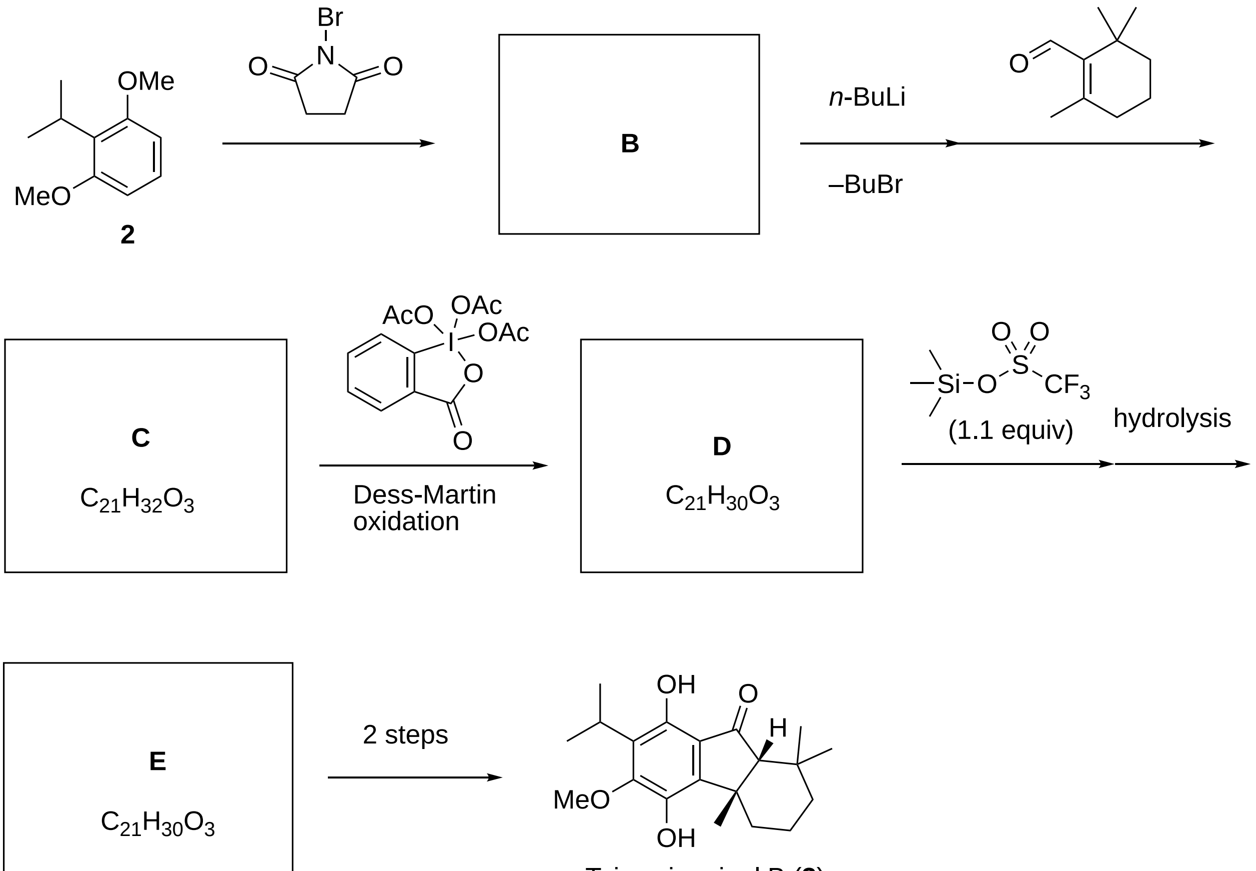
(i)



(j)



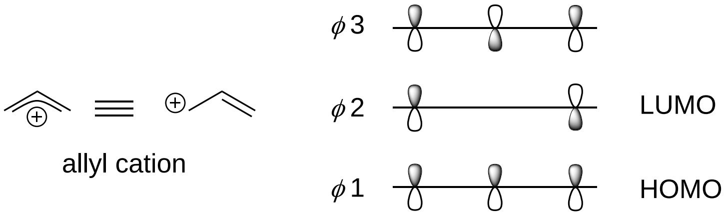
2. Compound **2** is transformed into Taiwaniaquinol (**3**) using a Nazarov cyclization as a key step. **Draw** the structures of **B**, **C**, **D**, **E**.



Taiwaniaquinol B (**3**)

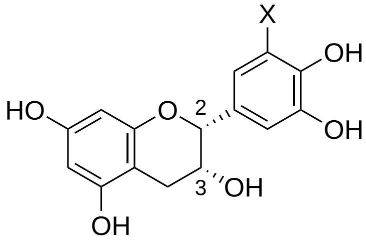
Optional problem:

The frontier molecular orbitals of the allyl cation, which consist of three carbon atoms and one π orbital shown below. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) are labeled in this figure. **Draw** the molecular orbitals of the pentadienyl cation using the same style as given in the example and **label** the LUMO and HOMO orbitals.

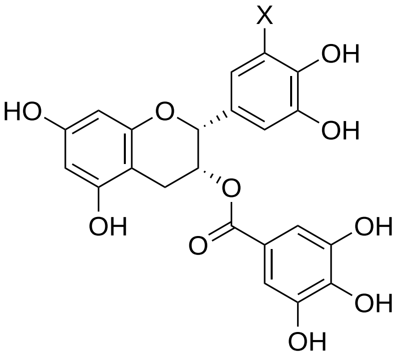


Problem 23. Tea party

In Japan, the cultivation of tea leaves and the green-tea culture started in the early 1200s. This culture has grown and developed ever since into the current form of the traditional 'tea ceremony', during which matcha is prepared and drunk. Moreover, regular green tea for daily consumption has become a staple of Japanese diet. Catechins, which are responsible for the characteristic taste of green tea, have been associated with a variety of health benefits. Tea leaves contain several catechins such as epicatechin, epigallocatechin, epicatechin gallate, and epigallocatechin gallate. Green tea also contains caffeine, which is bitter, and theanine, which adds a savory (umami) flavor.



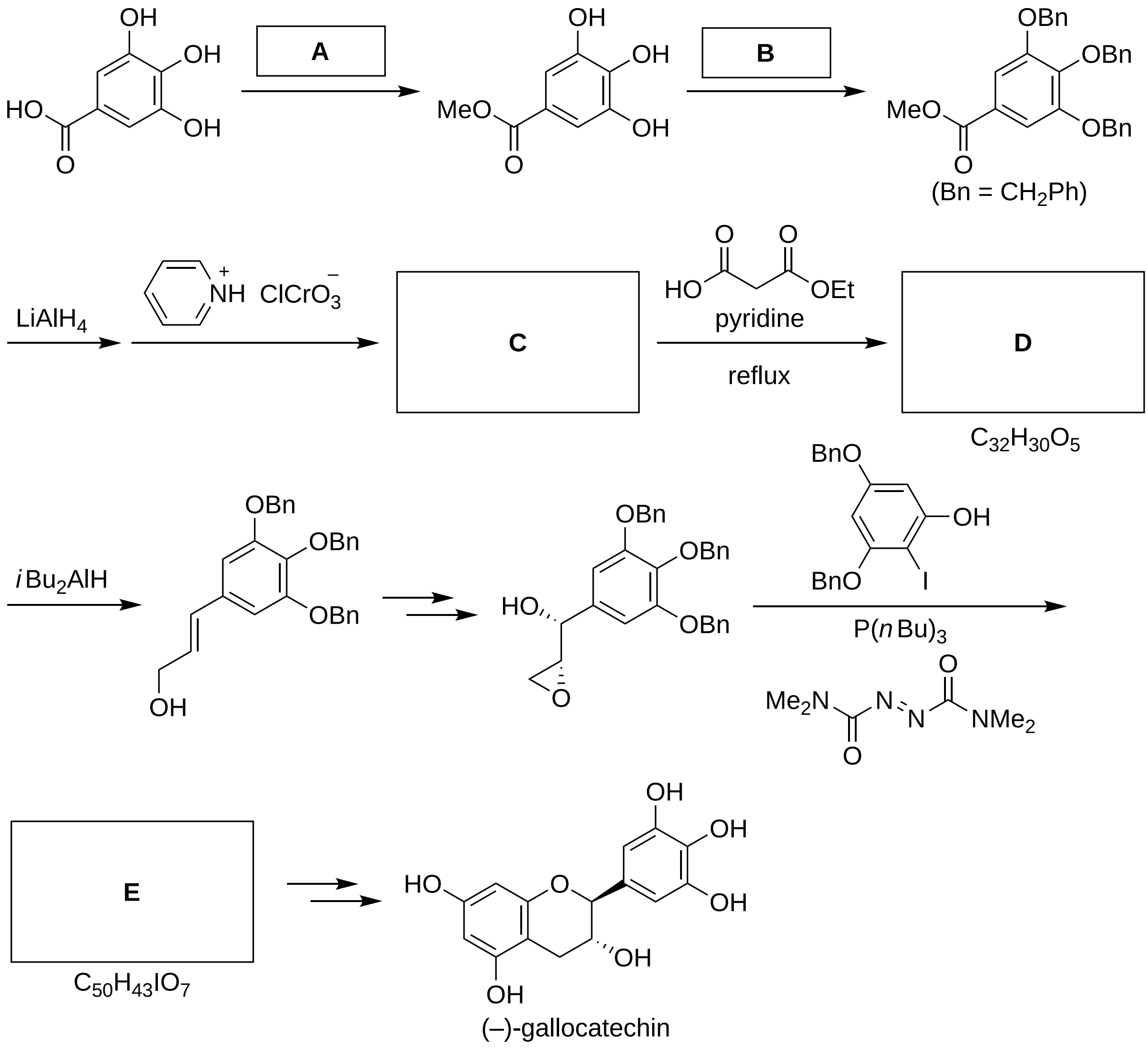
X = H: (–)-epicatechin
X = OH: (–)-epigallocatechin



X = H: (–)-epicatechin gallate
X = OH: (–)-epigallocatechin gallate

1. **Assign** the absolute configuration of the stereocenters at the 2- and 3-positions of (–)-epicatechin using the *R*/*S* nomenclature.

The following scheme shows a synthetic route to (–)-gallocatechin, which is an epimer of (–)-epigallocatechin.



2. From the following conditions, **choose** the best for **A**.

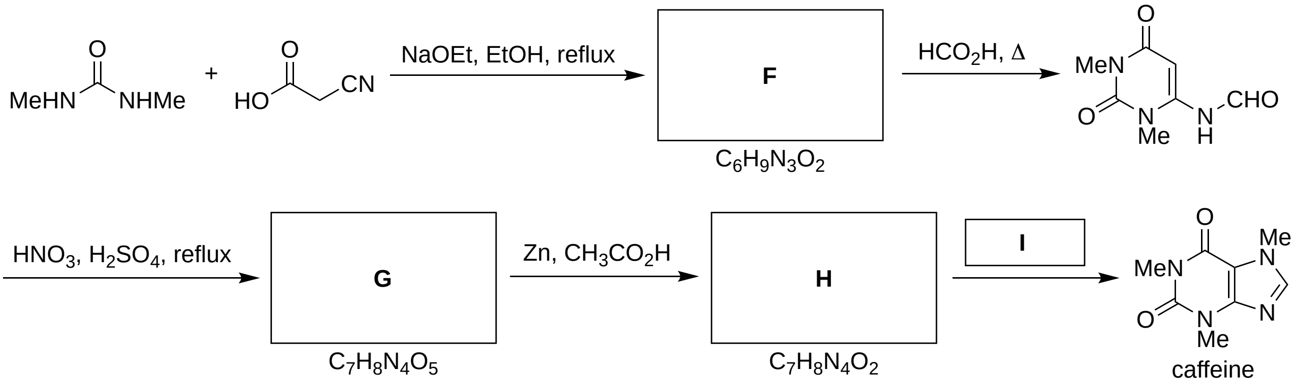
☐ MeMgBr, THF
☐ NaOMe, THF
☐ $NaBH_4$, MeOH
☐ HCl, MeOH

3. From the following conditions, **choose** the best for **B**.

☐ $PhCH_2OH$, NaH
☐ $PhCH_2Cl$, NaH
☐ PhCHO, HCl
☐ $PhCO_2H$, HCl

4. **Draw** the structures of **C–E** and clearly identify the stereochemistry where necessary.

Caffeine, which is responsible for the bitter taste of green tea, can be synthesized as follows.

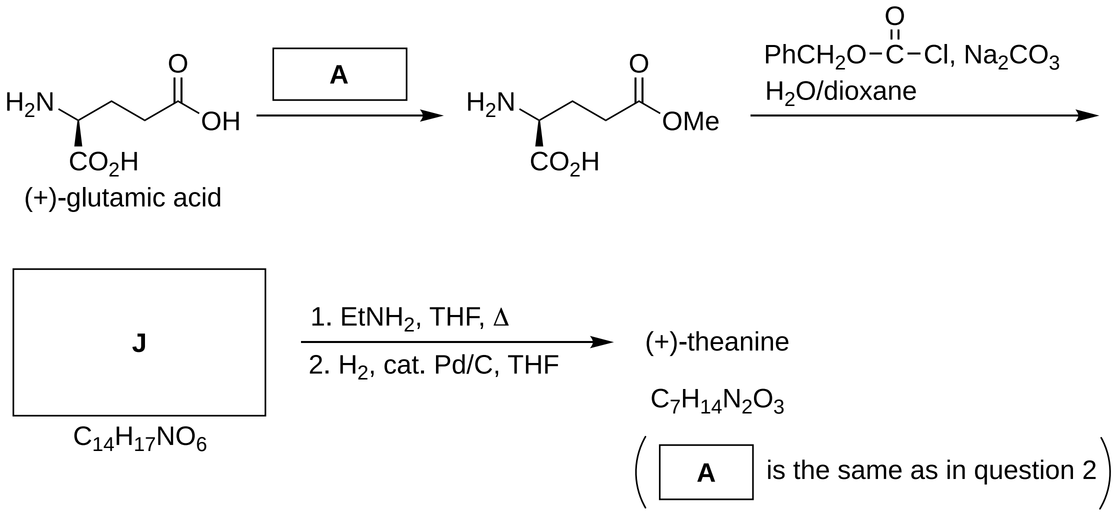


5. **Draw** the structures of **F–H**.

6. From the following conditions, **choose** the best for **I**.

☐ 1) NaH, 2) MeI
☐ 1) MeMgBr, 2) H_2O
☐ NaOMe, MeOH
☐ NMe_3, H_2O

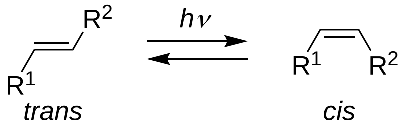
(+)-Theanine, which is responsible for the savory (umami) taste of green tea, can be synthesized from (+)-glutamic acid as follows.



7. **Draw** the structures of **J** and (+)-theanine and clearly identify the stereochemistry where necessary.

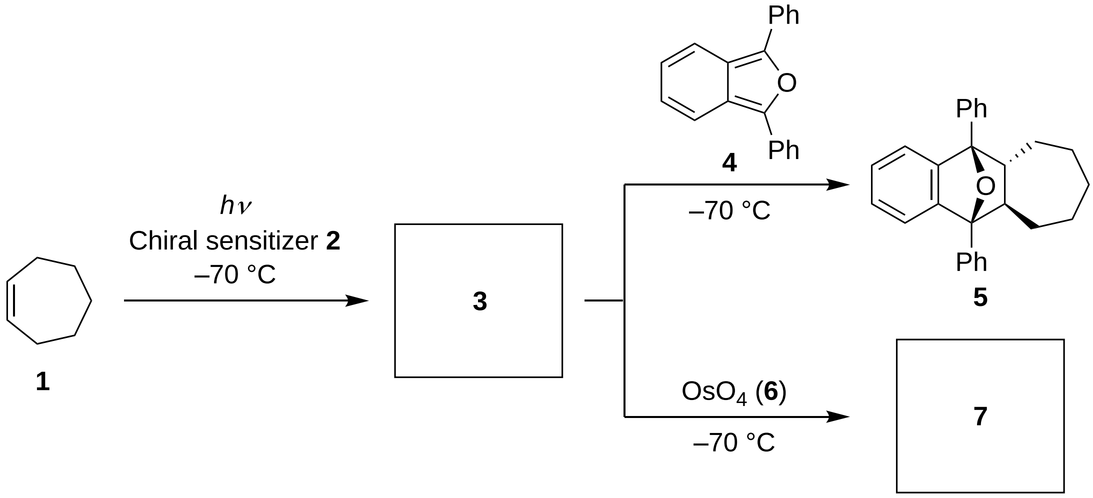
Problem 24. *E*-*Z* chemistry

Alkenes can undergo *trans*/*cis* isomerization upon photoirradiation as shown below, and the isomerization process can be accelerated by adding a sensitizer that is excited upon absorption of light and subsequently transfers this energy to the alkenes.

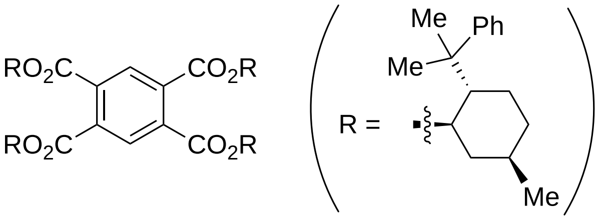


This photo-induced *trans*/*cis* isomerization also occurs in certain cycloalkenes, which contain connected substituents R^1 and R^2. In general, *trans*-cycloalkenes that contain a 7- to 9-membered ring are highly reactive due to their intrinsic ring strain. Their two faces of the π-plane can be distinguished by the reactivity, as one face is blocked by the carbon chain within the ring, while the other unblocked face can engage selectively in chemical reactions.

Moreover, asymmetric syntheses can be achieved by exposing cycloalkenes to irradiation in the presence of a chiral sensitizer. For instance, as shown in the scheme below, photoirradiation of cycloheptene (**1**) at low temperature in the presence of chiral sensitizer **2** generates **3**, which undergoes a Diels–Alder reaction with 1,3-diphenylisobenzofuran (**4**) to enantioselectively afford optically active **5**. Under the same photoirradiation conditions, the reaction of **3** with OsO_4 (**6**) results in the formation of optically active **7**.

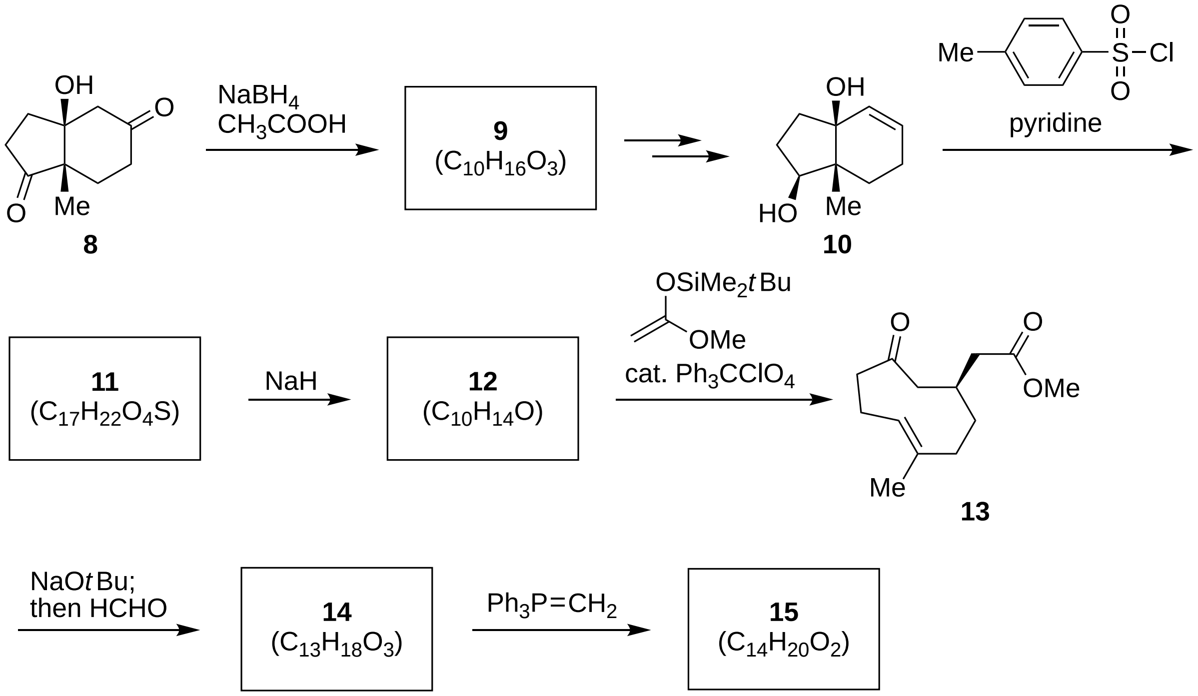


Chiral sensitizer **2**:

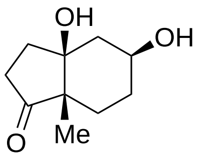


1. **Draw** the structures of **3** and **7** and clearly identify the stereochemistry where necessary.

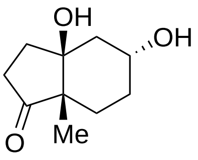
The naturally occurring compound Coraxeniolide is a bicyclic compound that contains fused 9- and 6-membered rings. A synthetic route to Coraxeniolide precursor **15** is shown below, starting from **8** via cycloalkene derivative **12**.



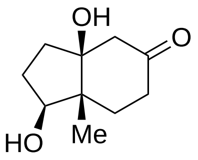
2. A nucleophilic addition to a carbonyl group does not occur easily when the carbonyl group is connected to a bulky substituent. When the two faces of the carbonyl group can be differentiated by the bicyclic structure as in **8**, the addition of the nucleophile usually occurs selectively from the outer face of the core structure. Based on these general considerations, **choose** the most suitable structure for **9** from **A**–**D**.



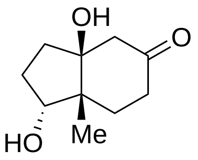
A



B



C



D

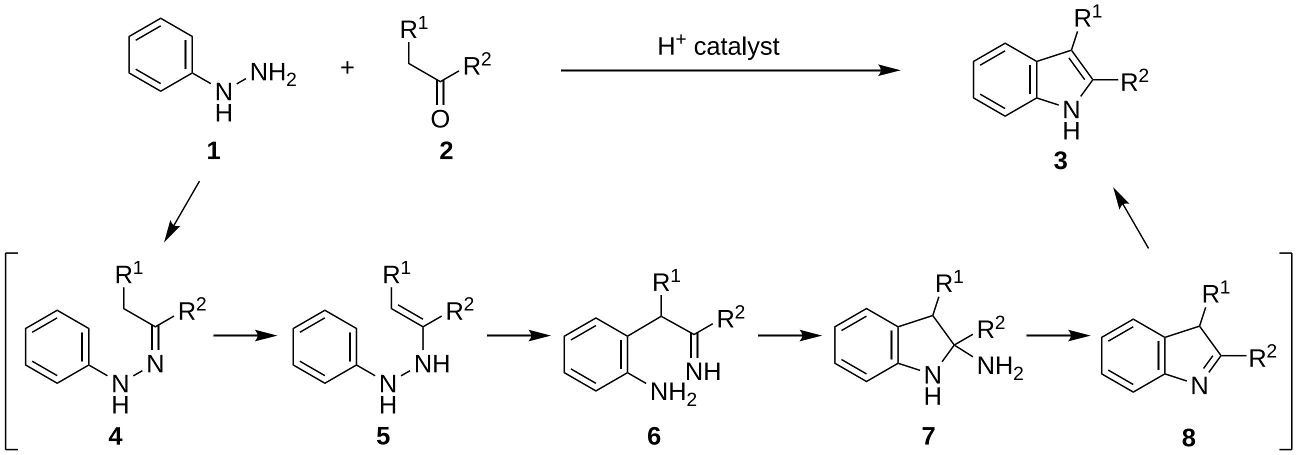
3. The nucleophilicity of the hydroxy group in alcohols generally increases with decreasing size of the associated alkyl group. **Draw** the structure of **11** and clearly identify the stereochemistry where necessary.

4. Compound **12** is a chiral compound although it does not possess a carbon stereocenter. **Draw** the structure of **12** and clearly identify the stereochemistry where necessary.

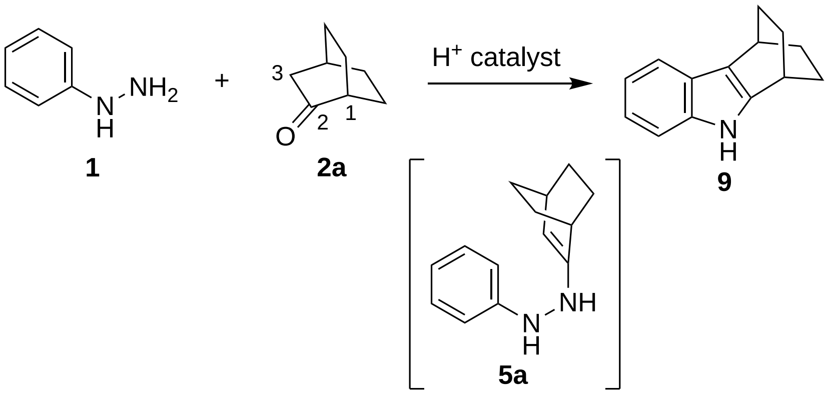
5. **Draw** the structures of **14** and **15** and clearly identify the stereochemistry where necessary.

Problem 25. Fischer indole synthesis

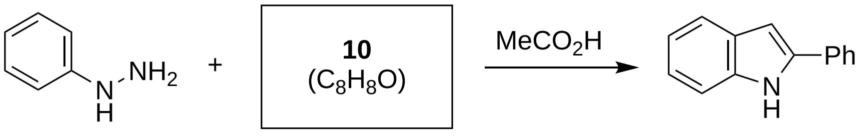
The reaction of phenylhydrazone **1** and carbonyl compound **2** under acid catalysis to give indole **3** via **4**–**8** is known as the Fischer indole synthesis.



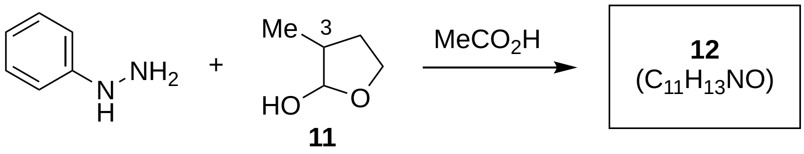
When bicyclic ketone **2a** is used as the carbonyl compound, indole **9** is obtained selectively via intermediate **5a**, wherein a carbon–carbon double bond is formed between C2 and C3 in order to avoid the formation of a highly strained carbon–carbon double bond between bridge-head C1 and C2.



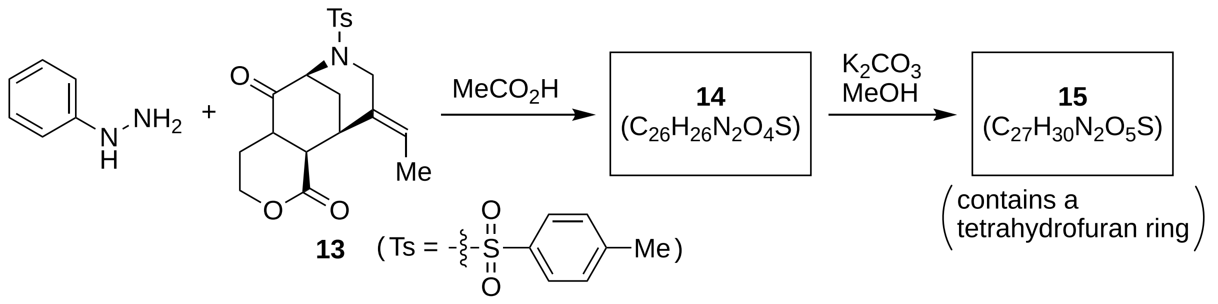
1. **Draw** the structure of compound **10** in the following reaction.



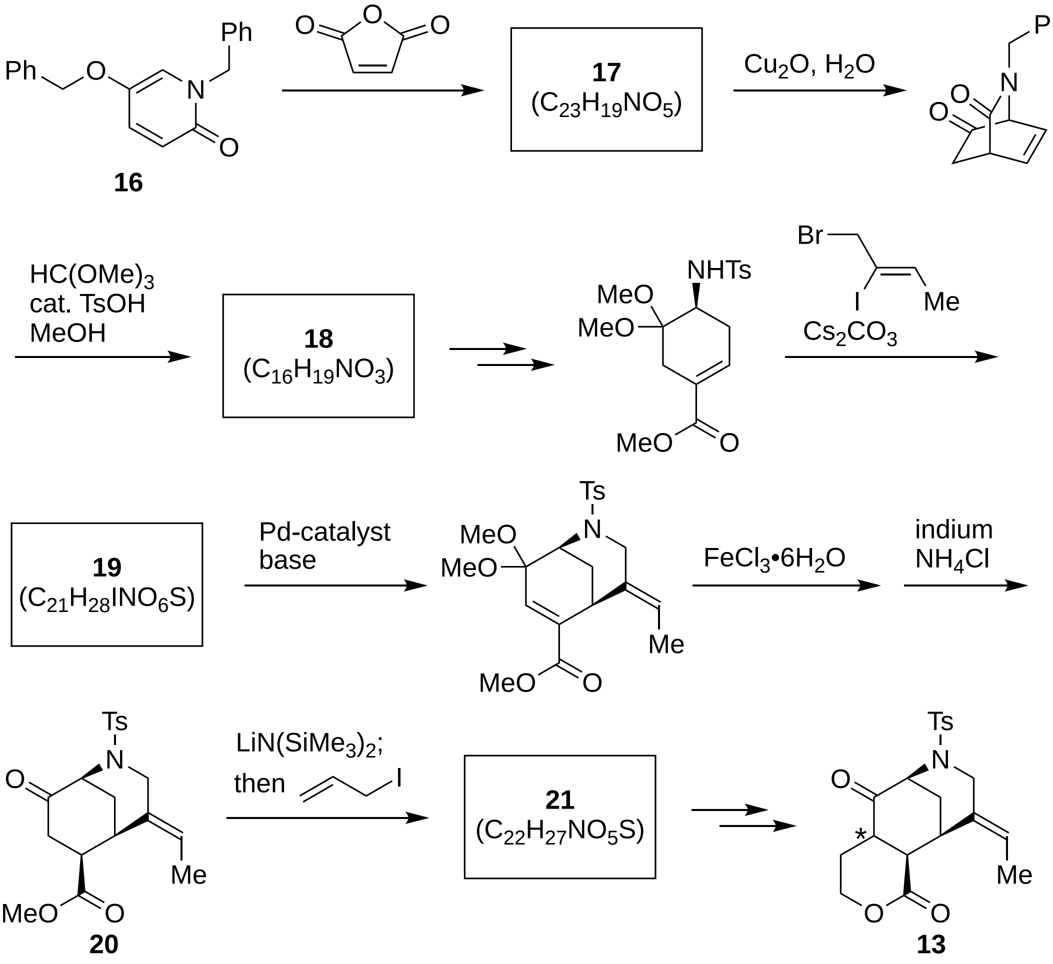
2. In the following reaction, tricyclic **12** is produced instead of an indole due to the substituent at the 3-position of **11**. **Draw** the structure of **12**.



3. **Draw** the structures of **14** and **15** in the following scheme and clearly identify the stereochemistry where necessary.



Compound **15** described above is a precursor for the naturally occurring Aspidophylline A, and **13** can be synthesized from **16** as shown below.



4. **Draw** the structures of **17** and **18** and clearly identify the relative stereochemistry where necessary.

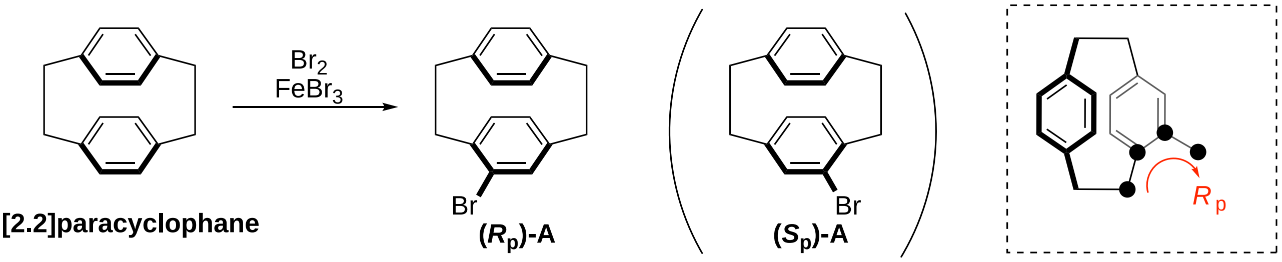
5. **Draw** the structure of **19** and clearly identify the stereochemistry where necessary.

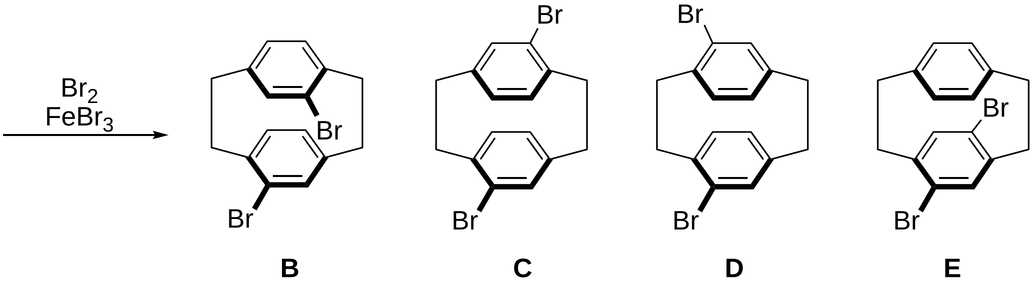
6. In the conversion of **20** to **21**, the reaction occurs selectively at the sterically less hindered side, and the stereochemistry with asterisk (*) of **13** is set in this step. **Draw** the structure of **21** and clearly identify the stereochemistry where necessary.

Problem 26. Planar chirality

A cyclophane consists of aromatic units (typically benzene rings) and aliphatic chains that form bridges between two non-adjacent positions of the aromatic rings. As shown below, if the bridge is ethylene ($-CH_2-CH_2-$) and the substitution pattern is *para*, it is called [2.2]paracyclophane. For some kinds of [2.2]paracyclophanes, enantiomers can be isolated depending on the substituent configurations on the aromatic rings given that these cannot rotate.

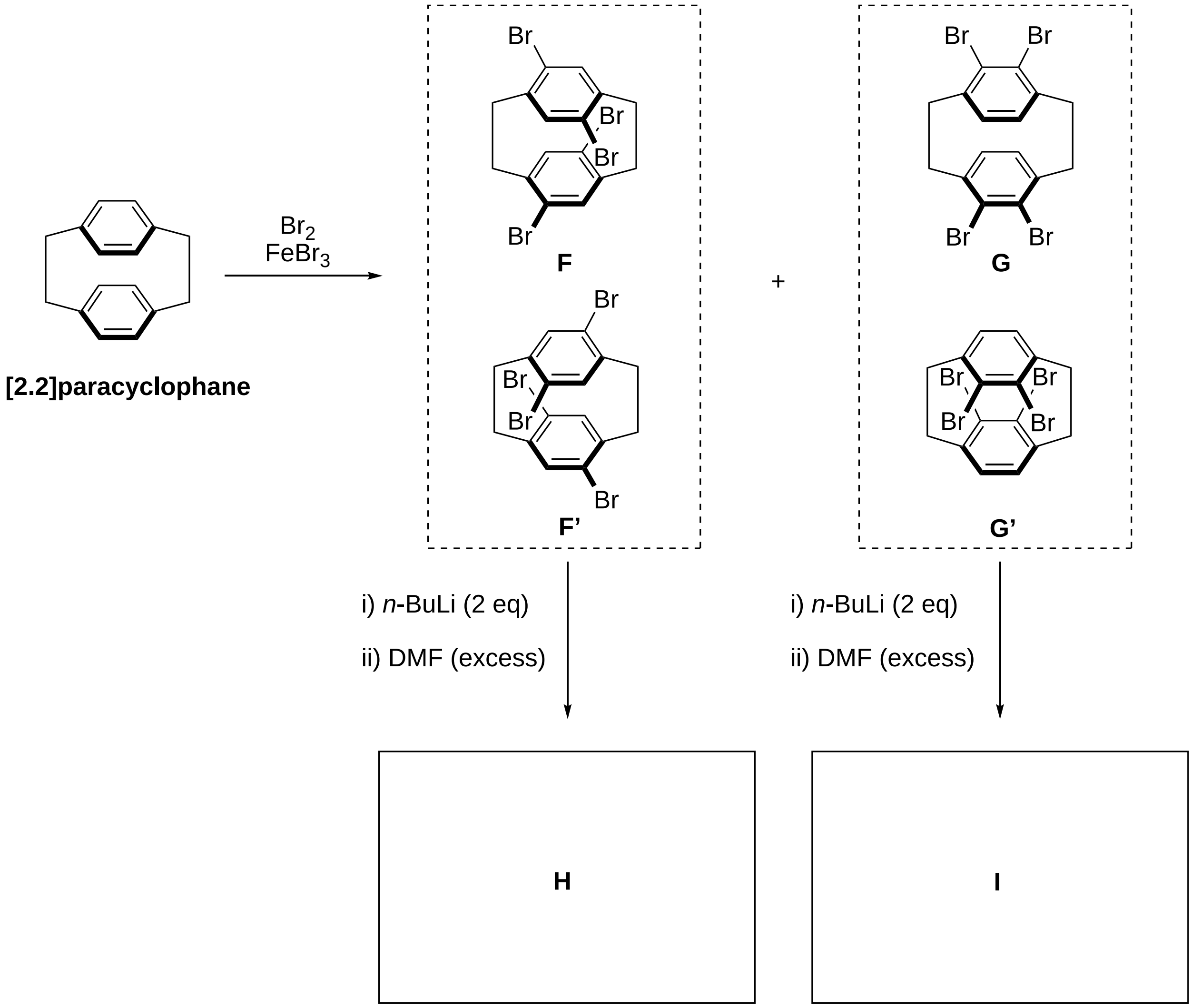
Brominating [2.2]paracyclophane affords mono-brominated **A**, which exhibits planar chirality, i.e., (R_p)- and (S_p)-isomers. Here, as shown in the dotted square, the definition of (R_p) is that the *ortho*-substituent is oriented in clockwise direction when traced from the other aromatic unit through the ethylene bridge. Further bromination of **A** furnished dibrominated products **B-E**.





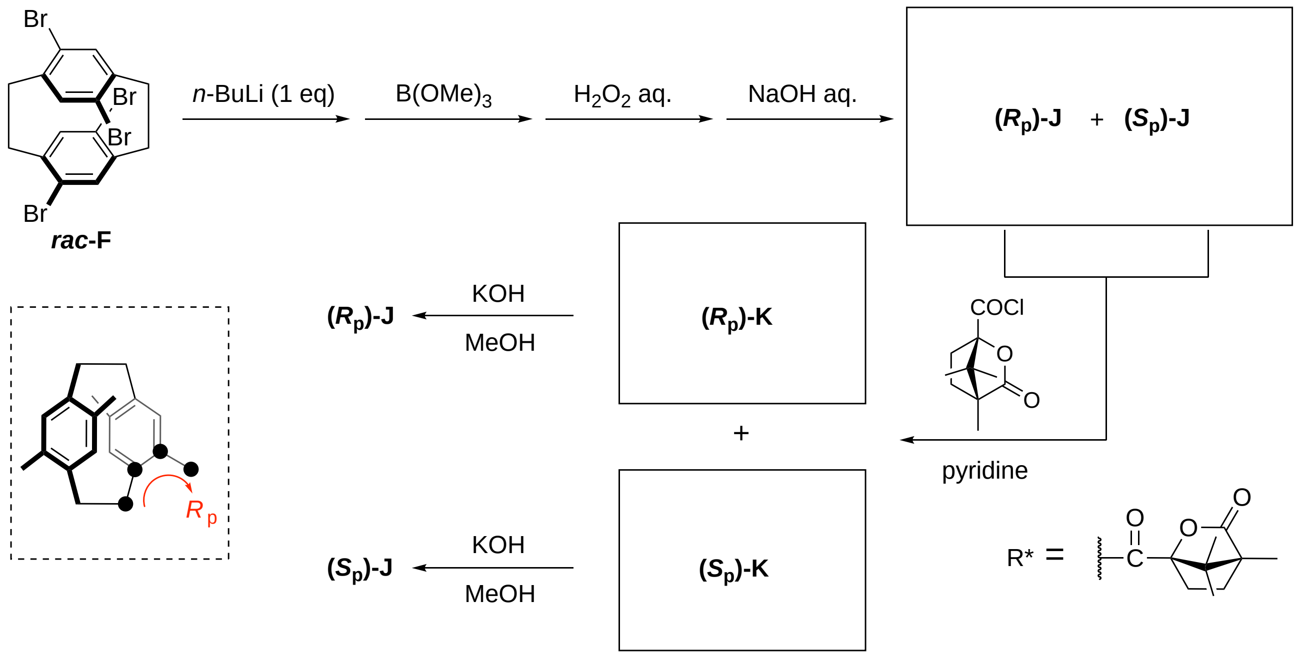
1. **Choose** from **B-E** all products that are optically active.

Bromination of [2.2]paracyclophane with an excess of bromine in the presence of $FeBr_3$ results in dibromination on each benzene ring to generate tetrabrominated products **F** (**F'**) and **G** (**G'**). Note that **F** and **F'** are a pair of enantiomers, while **G** and **G'** are identical. By adding two equivalents of *n*-BuLi to a solution of **F** or **G** at low temperature, one of two bromo-substituents in each benzene unit is exchanged to lithium, and the subsequent addition of an excess of DMF leads to the formation of several products.



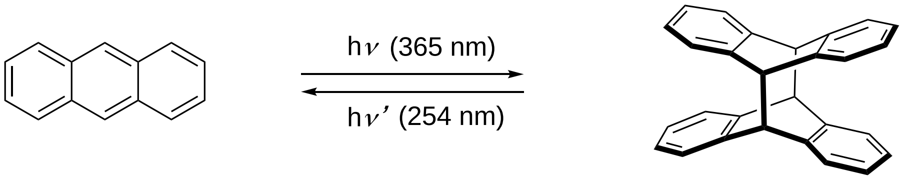
2. Assuming that the reaction proceeds completely, **draw** all the possible stereoisomers for **H** and **I**.

A racemate of tetrabrominated **F** (***rac*-F**) is transformed into **J** by applying the reaction conditions shown below. Here **J** is a racemic mixture of (R_p)-**J** and (S_p)-**J**. The racemic mixture reacts with optically active (-)-camphanic chloride to give a diastereomeric mixture of (R_p)-**K** and (S_p)-**K**, which can be separated by column chromatography. (R_p)-**K** and (S_p)-**K** can be hydrolyzed to give optically pure (R_p)-**J** and (S_p)-**J**. Here, the definition of (R_p) is the same as in Q1. When there are several kinds of substituents on the benzene ring, the definition obeys the Cahn-Ingold-Prelog priority rule.

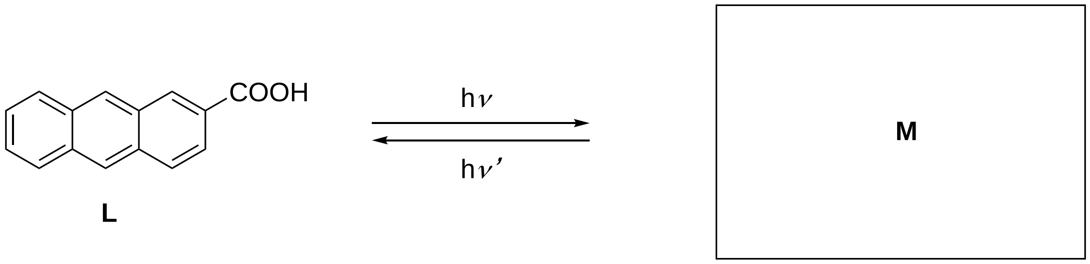


3. **Draw** the structures of (R_p)-**J**, (S_p)-**J**, (R_p)-**K**, and (S_p)-**K**. You can abbreviate the acyl moiety derived from (-)-camphanic chloride as R*.

The photodimerization of anthracene affords product whose planar chirality is similar to that of cyclophanes. As shown below, anthracene undergoes photodimerization under irradiation with ultraviolet light.

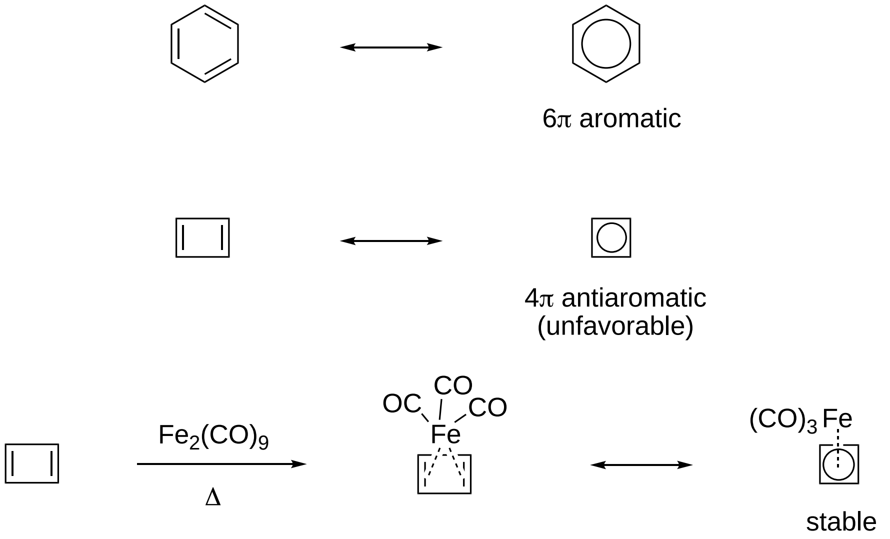


4. **Draw** all the stereoisomers of photodimerized products of 2-substituted anthracene **L**. Among these, **draw** lines between each pair of enantiomers.

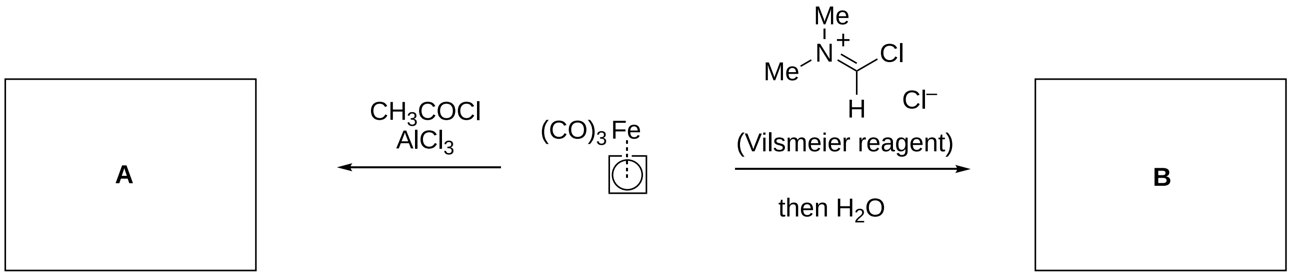


Problem 27. Cyclobutadiene

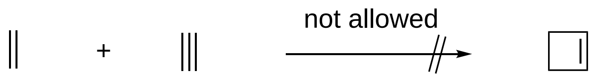
In contrast to benzene, cyclobutadiene adopts a rectangular conformation in order to avoid 4π antiaromaticity by bond alternation. Even though it is difficult to isolate pristine cyclobutadiene under ambient conditions, its tricarbonyliron complex is isolable and relatively stable toward acids and bases. Moreover, this complex readily engages in electrophilic substitutions, *i.e.*, it exhibits reactivity that is similar to that of benzene.

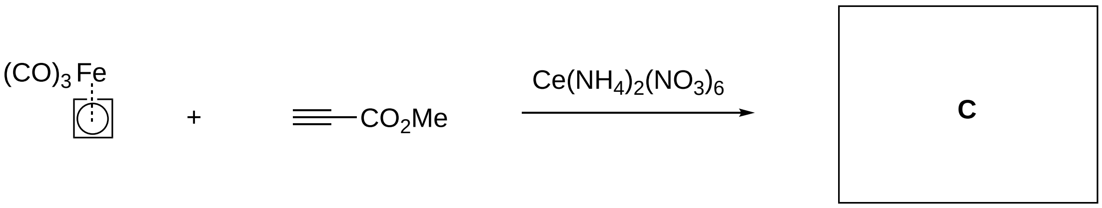


1. **Draw** the structures of **A** and **B**, which are obtained from cyclobutadiene under the conditions shown below. The description of the iron complex is allowed to be the same as that of substrate.

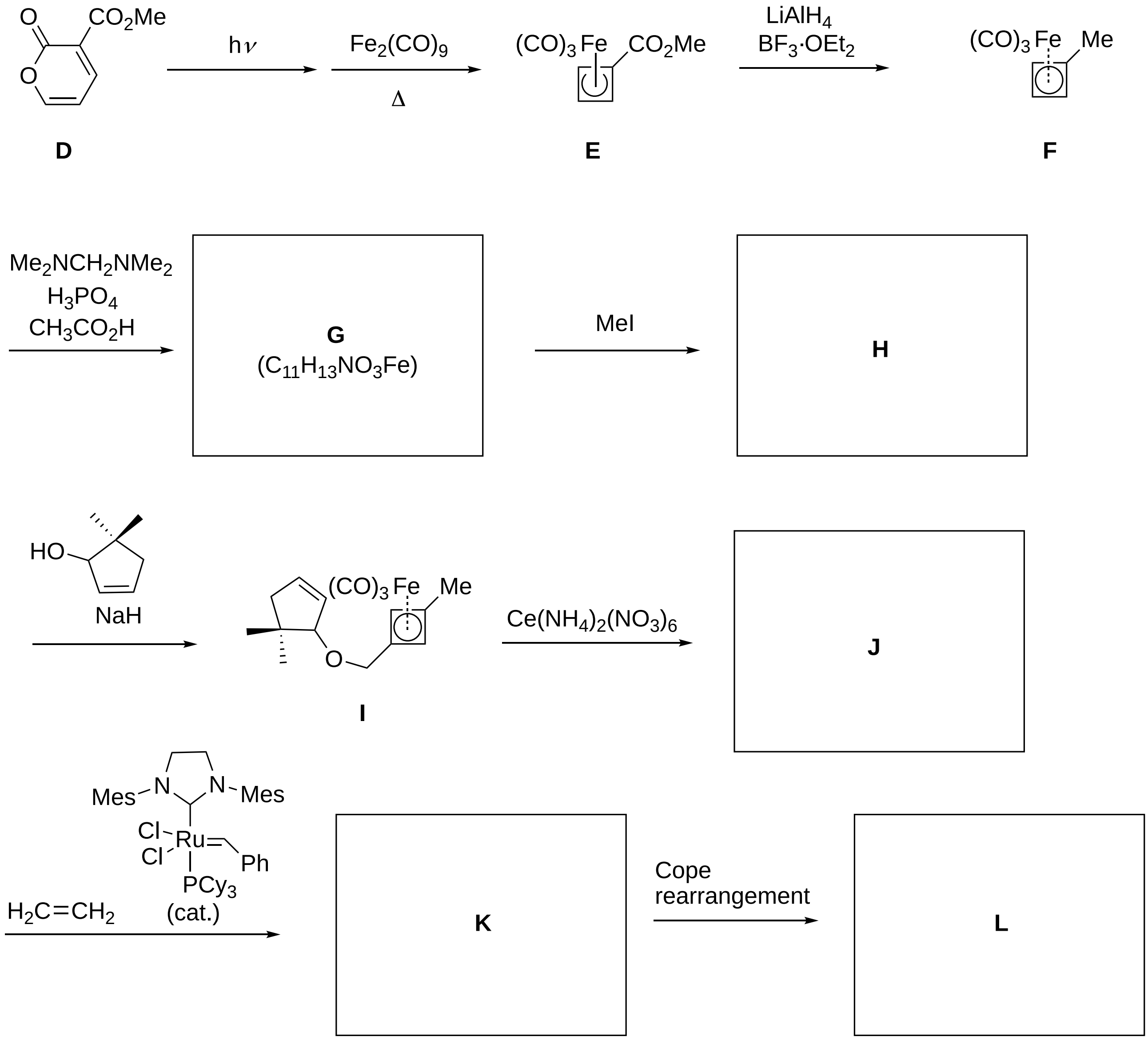


2. The iron moiety can be removed by treatment with cerium ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$. Although [2+2]-cycloaddition reactions are generally not allowed, the thus generated cyclobutadiene is so reactive that it can undergo [2+2]-cycloaddition-like reactions with alkenes and alkynes. **Draw** the structure of **C** shown below. Its stereochemistry is not required.





3. A part of a synthetic route toward natural product asteriscanolide is shown below.



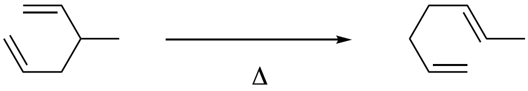
3-1. **Draw** the structure of the aromatic compound obtained by heating a mixture of **D** and dimethyl acetylenedicarboxylate.

3-2. **Draw** the structures of **G** and salt **H**. The latter is an intermediate of the reaction from **G** to **I**.

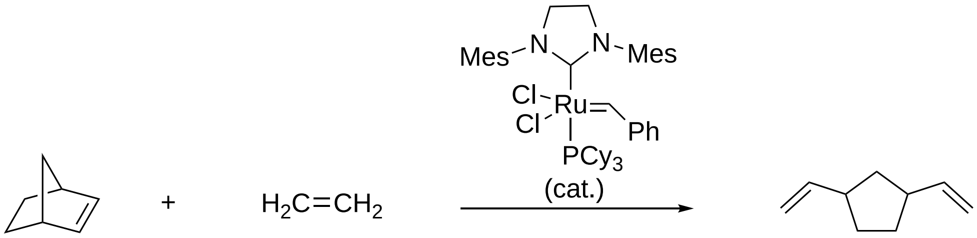
3-3. **Draw** the structure of tetracyclic compound **J** (its stereochemistry is not required).

3-4. The ring opening metathesis of **J** furnishes **K**, and the subsequent Cope rearrangement leads to the formation of **L**. **Draw** the structures of tricyclic compounds **K** and **L** (their stereochemistry is not required). Examples of Cope rearrangement and ring-opening metathesis are shown below.

Cope rearrangement:

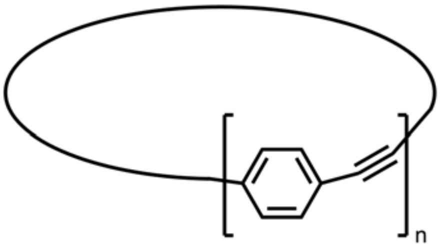


Ring-opening metathesis :

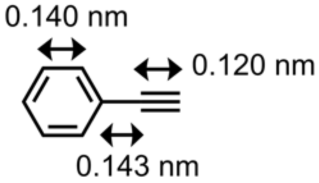


Problem 28. Onion-like complexes

As shown below, cyclic molecules composed of alternating benzene and alkyne moieties can form an onion-like concentric complex if a suitable pair of ring-sizes is chosen.



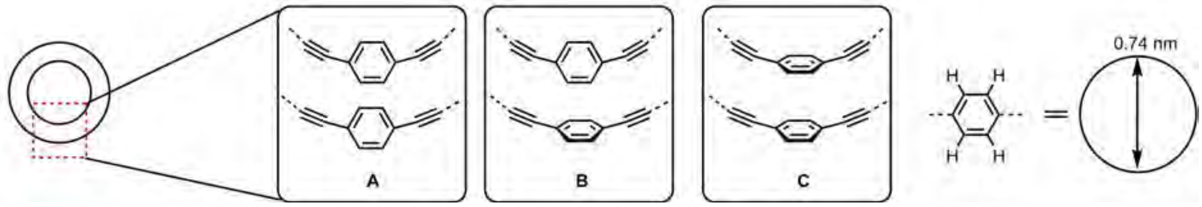
1. For $n = 6$, **calculate** the length of the outer perimeter of the ring-shaped molecule. A list of relevant bond-length values is shown below. Consider the benzene ring as a regular hexagon. In addition, **calculate** the diameter under the assumption that the ring is a true circle.



2. For $n = 9$, **calculate** the length of the outer perimeter and the diameter under the same assumptions as in Q1.

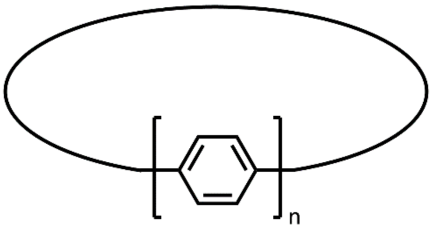
3. Ring **1** (n = 6) and ring **2** (n = 9) can form a concentric complex in chloroform. **Calculate** the width of the interspace between the two rings (ignore the volume of the atoms).

4. From **A**-**C** shown below, **choose** all the possible configurations of the benzene rings in the complex of **1** and **2** when viewed vertically relative to the ring plane. Here, a benzene ring is regarded as a circle with a diameter of 0.74 nm.



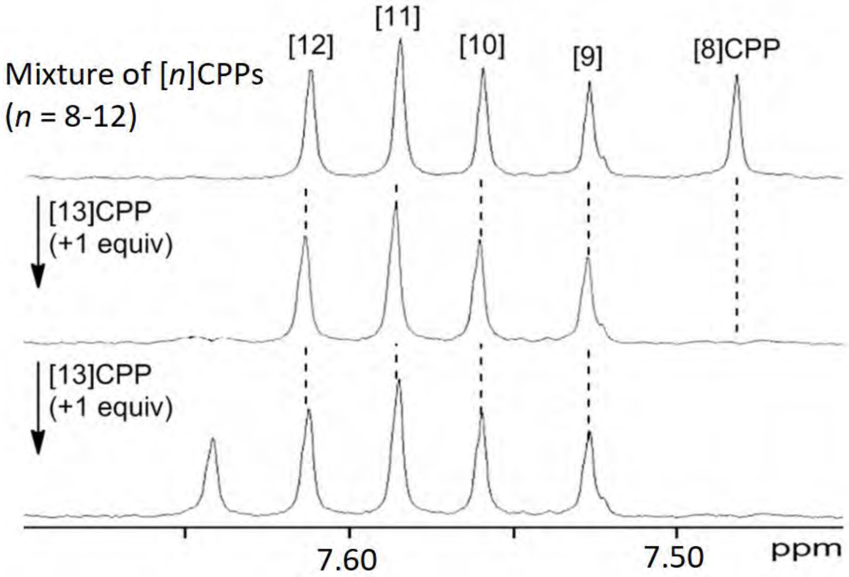
5. Similar to the case of the encapsulation of **1** by **2**, C_{60} can be encapsulated by ring **1**. **Estimate** the diameter of C_{60} under the same assumptions for **1** and **2** regarding the interspace.

Cycloparaphenylenes (CPPs) are ring-shaped molecules that consist exclusively of benzene moieties that are connected in a *para* fashion. Depending on the number of constituent benzene rings (*n*), CPPs are usually denominated [*n*]CPP. There are combinations of [*n*]CPPs that can form onion-like concentric complexes.



6. A free-energy change of –18.00 kJ mol^{-1} was estimated for the encapsulation of [6]CPP by [11]CPP in deuterated dichloroethane at 323.15 K. **Calculate** the concentration of free [6]CPP (which does not form any complexes) when the same volume of solutions of [6]CPP and [11]CPP in deuterated dichloroethane (0.800 mmol L^{-1} each) is mixed at 323.15 K. In this case, the resulting mixture is homogenous.

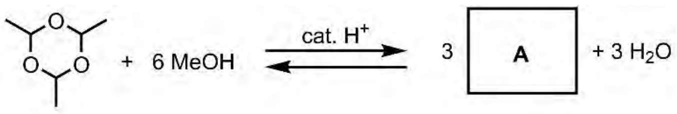
7. Two equivalents of [13]CPP in solution were added in two portions to a solution containing an equimolar amount of five kinds of [*n*]CPPs (*n* = 8 – 12). Shown below is the ^{1}H NMR spectral change. No signals derived from CPPs were observed outside the region shown. Upon adding the first equivalent of [13]CPP, the formation of a precipitate was observed. Based on the information given, **choose** all correct statements among (a) – (e).

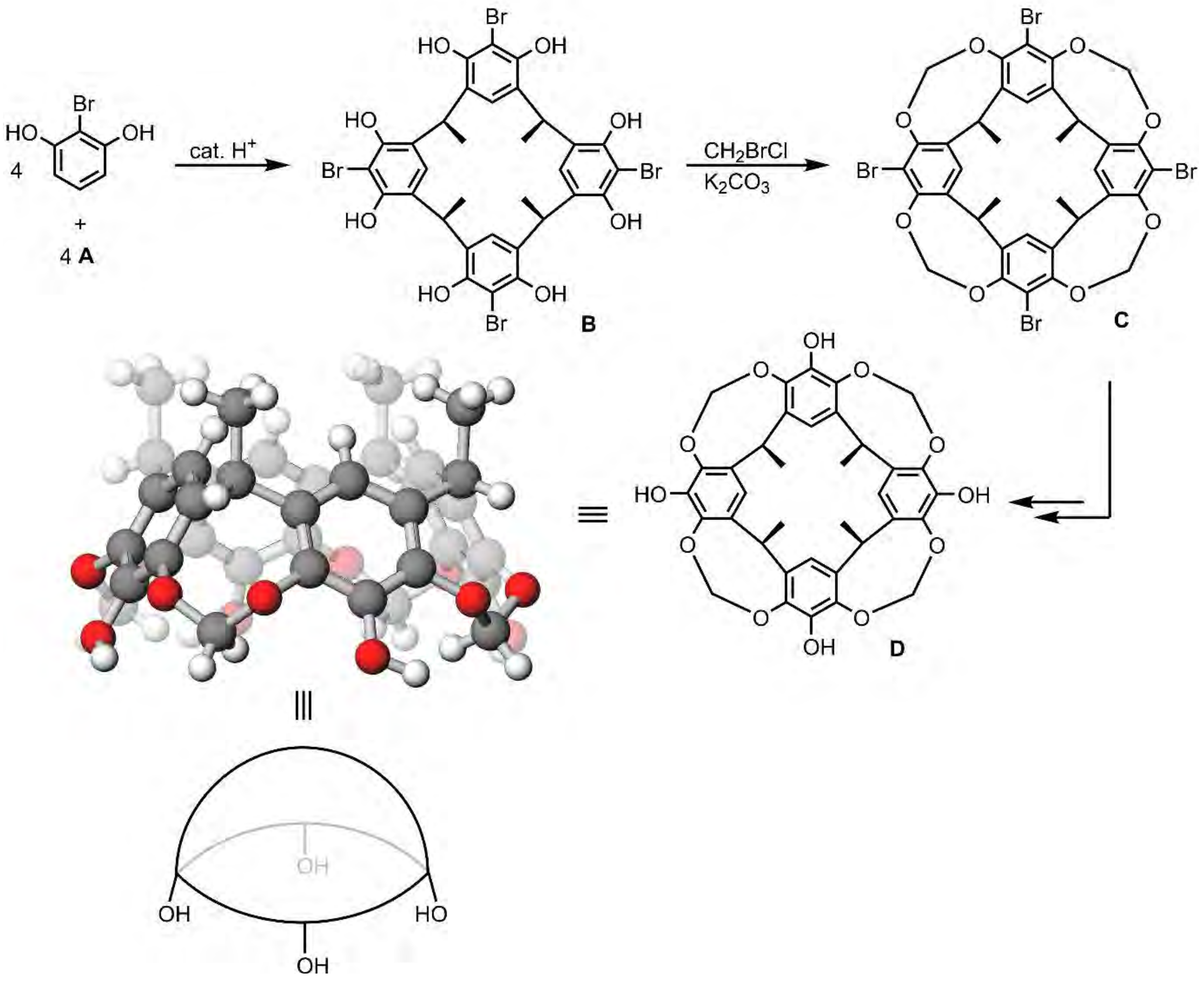


(a) [13]CPP encapsulates [8]CPP to form a precipitate.
(b) [13]CPP quantitatively forms complexes with all other [*n*]CPPs (*n* = 8 – 12) and generates a precipitate.
(c) The new peak that emerges at approximately 7.64 ppm can be ascribed to the complex of [13]CPP and [8]CPP.
(d) The new peak that emerges at approximately 7.64 ppm can be ascribed to [13]CPP.
(e) In the presence of [13]CPP, the peak associated with [8]CPP is substantially downfield shifted.

Problem 29. Hydrogen-bonded capsules

Calix[4]arene is a bowl-shaped molecule that is synthesized as shown below.



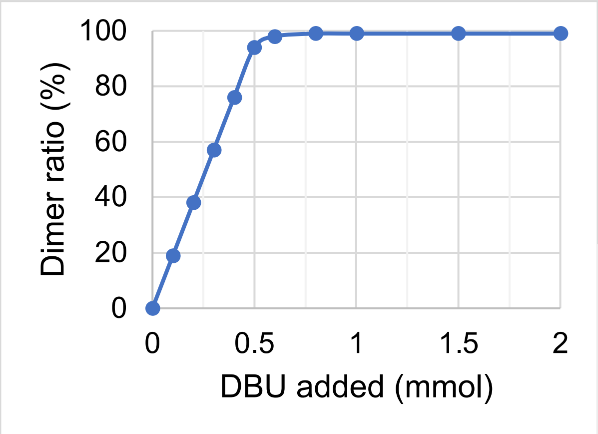


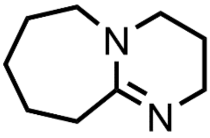
1. **Draw** the structure of intermediate **A**.

2. **Choose** the most suitable conditions for the transformation from **C** to **D**.

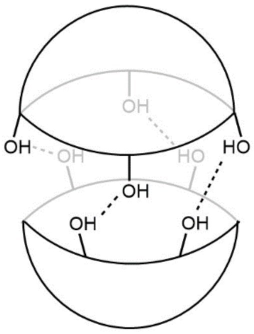
   (a) *t*BuLi, then $B(OMe)_3$, then AcOH
   (b) *t*BuLi, then $B(OMe)_3$, then H_2O_2/NaOH aq.
   (c) BBr_3, then H_2O_2/NaOH aq.
   (d) PMe_3, then H_2SO_4
   (e) PMe_3, then H_2O_2 aq.

3. Two molecules of **D** form an aggregate via hydrogen-bonds upon addition of DBU (a kind of weakly nucleophilic but strong organic base; see the structure below) to a chloroform solution of **D**. Among (a) – (d), **<u>choose</u>** the most probable structure for the dominant hydrogen-bond network of dimers of **D**. Refer to the graph showing the ratio of dimer (%) as a function of the amount of DBU added to a solution of **D** (0.25 mmol) in chloroform.

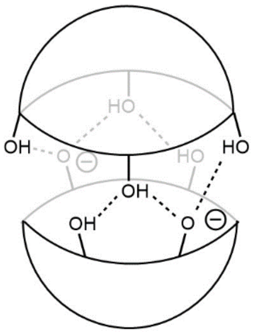




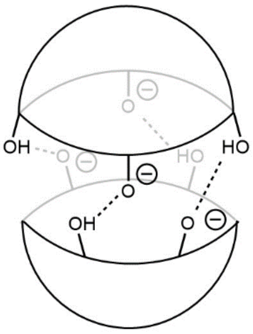
DBU



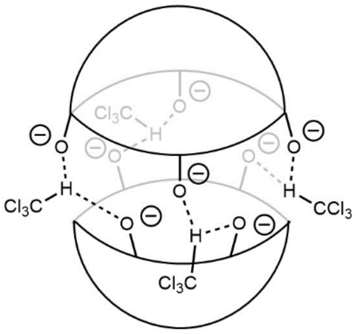
(a)



(b)



(c)



(d)

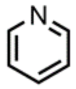
The dimeric capsule of **D** (host) described in Q3 can encapsulate other molecules (guests). In solution, the encapsulation and release of the guest(s) are reversible. The association constant K for this process is given by

$$K = \frac{[solvent][guest@host]}{[solvent@host][guest]}$$

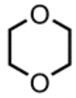
Here, the encapsulation of guest **A** by host **B** is expressed as **A@B**. The relative association constant K_{rel} can be calculated by measuring the ratio of free and encapsulated guests in the coexisting state. Thus, K_{rel} is given by

$$K_{\mathrm{rel}} = \frac{K_2}{K_1} = \frac{[solvent][guest2@host]}{[solvent@host][guest2]} / \frac{[solvent][guest1@host]}{[solvent@host][guest1]} = \frac{[guest2@host][guest1]}{[guest1@host][guest2]}$$

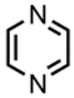
Below, the K_{rel} values of several guest molecules in chloroform relative to benzene (guest1) are shown.



pyridine
9.6



1,4-dioxane
77



pyrazine
1300

In the presence of a sufficient amount of DBU, **D** dimerizes almost quantitatively. In the following questions, free **D** can be ignored.

4. Equimolar amounts of pyrazine and 1,4-dioxane are added to a chloroform solution of **D** in the presence of excess DBU. After the system reaches the equilibrium state, a 75:25 ratio of free to encapsulated 1,4-dioxane was found. **Estimate** the ratio of pyrazine encapsulated by **D**.

5. A chloroform solution of dimers of **D** encapsulating benzene is exposed to the following conditions (a) and (b). For each set of conditions, **choose** from (1) – (3) what happens to the capsule structure and the benzene molecule.

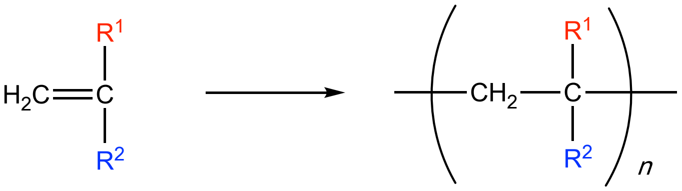
   (a) Addition of acetyl chloride and pyridine.
   (b) Dilution with chloroform.

   (1) The capsule dissociates and benzene is released.
   (2) Both capsule and benzene remain intact.
   (3) The capsule remains intact, but benzene is released.

6. The same solution used in Q5 is treated with K_2CO_3 and CH_2BrCl (*cf.* the reaction **B→C** in the scheme on the first page of this problem). Subsequently, pyrazine, which is more prone to be encapsulated than benzene, is added. However, an exchange between the encapsulated benzene and pyrazine is not observed. **Explain** this observation.

Problem 30. Synthesis and structural analysis of polymers

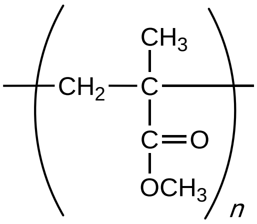
Polymers that contain carbon-carbon based main chains are often synthesized by chain polymerization of vinyl monomers (Eq. 1).



$$H_2C{=}C(R^1)(R^2) \longrightarrow \left(CH_2{-}C(R^1)(R^2) \right)_n$$

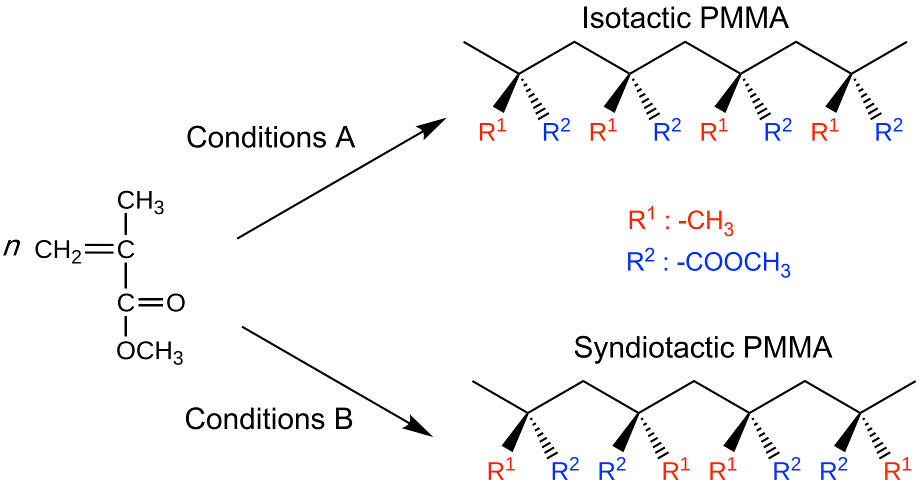
(Eq. 1)

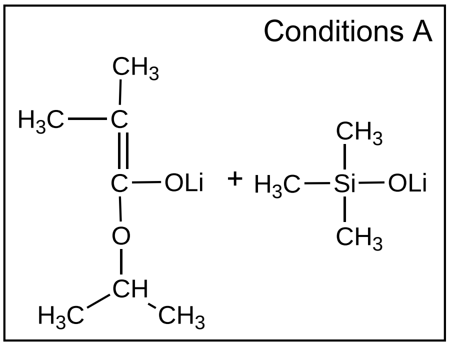
When the main chain of a polymer adopts a zigzag shape, polymers in which all substituents R^1 (or R^2) are located on the same side are called ‘isotactic’, while those in which the substituents are located on alternating sides of the main chain are called ’syndiotactic’. Polymers that contain R^1 = $-CH_3$ and R^2 = $-COOCH_3$ are called poly methyl methacrylate (PMMA). Isotactic PMMA is obtained under conditions A in the scheme below, while syndiotactic PMMA is obtained under conditions B.

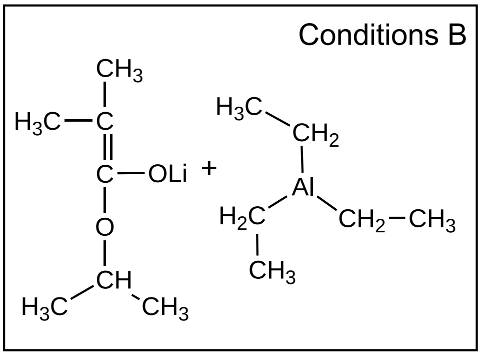


$$\left(CH_2{-}C(CH_3)(COOCH_3) \right)_n$$

Poly(methyl methacrylate) (PMMA)







The ^{1}H NMR spectra of isotactic and syndiotactic PMMA are shown in Figure 1.

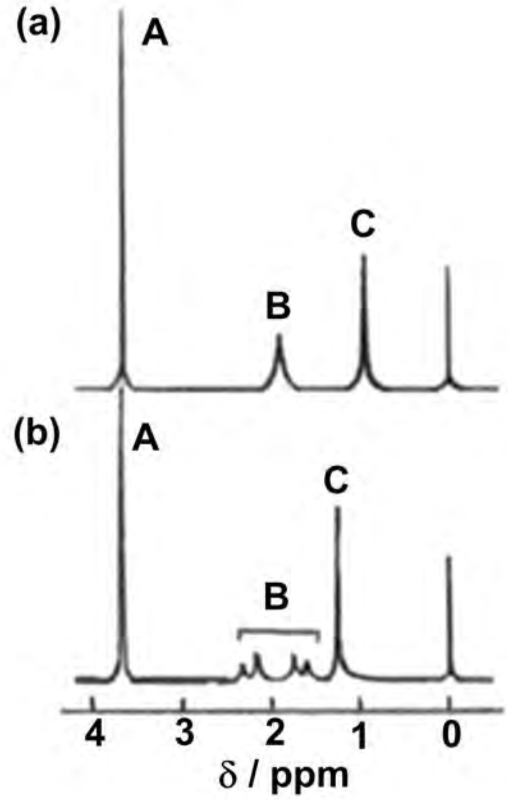


Figure 1. 100 MHz ^{1}H NMR spectra of two types of PMMA in CD_3NO_2 at 100 °C

1. In Figure 1, the intensity ratio of the peaks A, B, and C is 3:2:3. **Assign** the protons in PMMA to the corresponding peaks.

2. In Figure 1, which ^{1}H NMR spectrum belongs to isotactic PMMA? **Choose** (a) or (b).

Among the copolymers that consist of two types of monomers (M_1 and M_2), those in which the sequences of M_1 and M_2 are not ordered are called 'random copolymers', while those in which the two types of monomers are arranged alternately are called 'alternating copolymers'. When the monomers M_1 and M_2 are copolymerized, the composition and arrangement of the polymer are determined by the (relative) reactivity of M_1 and M_2. When the polymerization proceeds via a radical reaction, two active species at the growth end of the polymer chain and two monomer species reacting with the active species can be considered. There are four types of monomer-addition reactions to the growth end of the polymer as shown in Eqs. 3.1 – 3.4. Here, it is assumed that the reaction between the growth end of polymer and the monomers M_1 and M_2 depends on the radical species ($M_1\cdot$ and $M_2\cdot$) at the growth end of the polymer. When the concentrations of the radically active species of M_1 or M_2 at the polymer growth end and monomers M_1 and M_2 are expressed by $[M_1\cdot]$, $[M_2\cdot]$, $[M_1]$, and $[M_2]$, respectively, the reaction rates of reactions 3.1 – 3.4 are expressed as follows:

Reaction rate

$$\sim\!\sim\!\sim M_1\bullet + M_1 \xrightarrow{k_{11}} \sim\!\sim\!\sim M_1\bullet \qquad k_{11}\,[M_1\bullet]\,[M_1] \qquad \text{(Eq. 3.1)}$$

$$\sim\!\sim\!\sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim\!\sim\!\sim M_2\bullet \qquad k_{12}\,[M_1\bullet]\,[M_2] \qquad \text{(Eq. 3.2)}$$

$$\sim\!\sim\!\sim M_2\bullet + M_1 \xrightarrow{k_{21}} \sim\!\sim\!\sim M_1\bullet \qquad k_{21}\,[M_2\bullet]\,[M_1] \qquad \text{(Eq. 3.3)}$$

$$\sim\!\sim\!\sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim\!\sim\!\sim M_2\bullet \qquad k_{22}\,[M_2\bullet]\,[M_2] \qquad \text{(Eq. 3.4)}$$

These reactions take place at the reactive chain end terminating in either monomer ($M_1\cdot$ and $M_2\cdot$) with their reaction rate constants k. The consumption rates of M_1 and M_2 are expressed according to Eqs. 4.1 and 4.2:

$$-\frac{d\,[M_1]}{dt} = k_{11}\,[M_1\bullet]\,[M_1] + k_{21}\,[M_2\bullet]\,[M_1] \qquad \text{(Eq. 4.1)}$$

$$-\frac{d\,[M_2]}{dt} = k_{12}\,[M_1\bullet]\,[M_2] + k_{22}\,[M_2\bullet]\,[M_2] \qquad \text{(Eq. 4.2)}$$

In a steady state, where the radical concentration is constant during polymerization, the rate at which the active species $M_1\cdot$ at the polymer growth end changes to $M_2\cdot$ and the rate at which $M_2\cdot$ changes to $M_1\cdot$ are equal. The ratio of the consumption rates of M_1 and M_2 under such conditions are shown in Eq. 5 when $k_{11} / k_{12} = r_1$ and $k_{22} / k_{21} = r_2$. The reactivity ratio (r_1 or r_2) for each propagating chain end is defined as the ratio of the rate constant for addition of a monomer of the species already at the chain end to the rate constant for addition of the other monomer. These ratios are a measure of the tendency for one of the two monomers to show a preference for insertion into a growing chain in which the last inserted unit was the same, rather than the other monomer.

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]} \bullet \frac{r_1\,[M_1] + [M_2]}{[M_1] + r_2\,[M_2]} \qquad \text{(Eq. 5)}$$

3. What kind of polymers can be obtained when r_1 and r_2 adopt the values shown in (1), (2), and (3)? Among (**a** – **g**), **select** those that most appropriately depict the sequence and the ratio of the monomer-unit content in the polymer synthesized by mixing two different monomers in a 1:1 ratio. When the values of fraction of M_1 unit in the polymer (0 – 1.0) and the initial concentration ratio of M_1 to M_2 ($[M_1] / ([M_1] + [M_2])$; 0 – 1.0) are plotted on the vertical and horizontal axes, respectively, **select** among (A – F) those sequences that most accurately reflect the characteristics of the polymer obtained in each system.

(1) $r_1 = 1.0$, $r_2 = 1.0$
(2) $r_1 = 2.0$, $r_2 = 0.50$
(3) $r_1 = 0$, $r_2 = 0$

Sequence and ratio of the monomer-unit content in the polymer:

a ------------M_1-M_2-M_1-M_2-M_1-M_2-M_1-M_2-M_1-M_2-----------

b ------------M_1-M_1-M_1-M_1-M_1-M_1-M_1-M_1-M_1-M_1-----------

c ------------M_2-M_2-M_2-M_2-M_2-M_2-M_2-M_2-M_2-M_2-----------

d ------------M_1-M_1-M_2-M_1-M_2-M_1-M_1-M_1-M_2-M_1-----------

e ------------M_2-M_2-M_1-M_2-M_1-M_2-M_2-M_2-M_1-M_1-----------

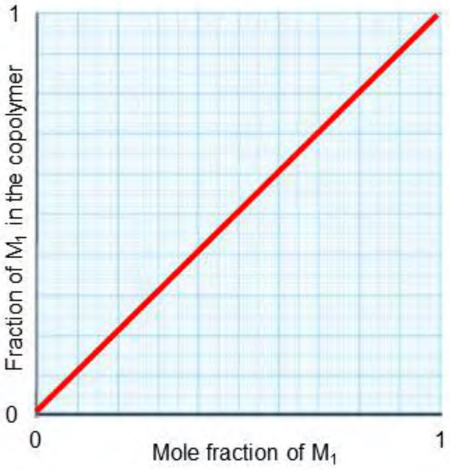
f ------------M_1-M_1-M_1-M_1-M_1-M_2-M_2-M_2-M_2-M_2-----------

g ------------M_1-M_2-M_2-M_1-M_1-M_2-M_1-M_2-M_2-M_1-----------

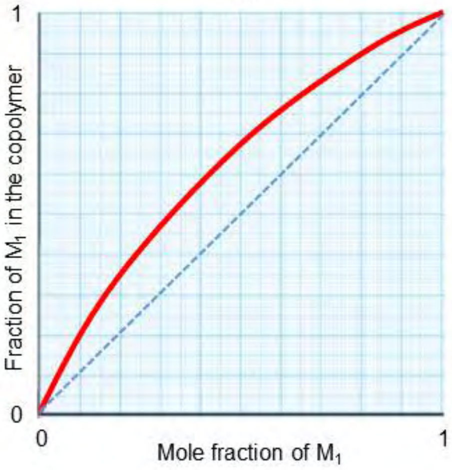
4. What kind of polymer can be obtained when $r_1 = 0.50$ and $r_2 = 0.50$? When the vertical axis is the fraction of M_1 in the polymer (0 to 1) and the horizontal axis is the initial concentration ratio of M_1 to M_2 (0 to 1), **select** a suitable graph showing the characteristics of the obtained polymer.

Graphs for Q3 and Q4

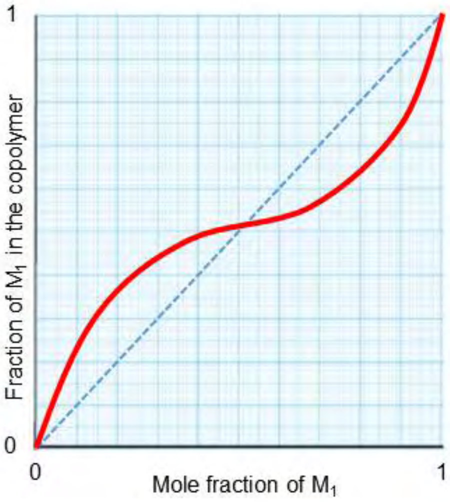
A



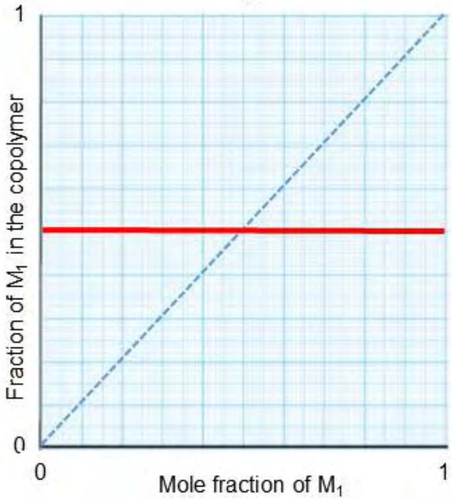
B



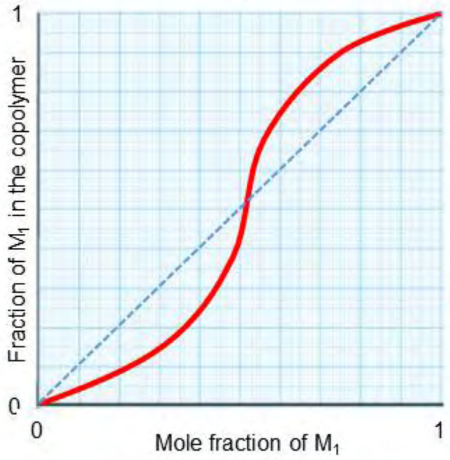
C



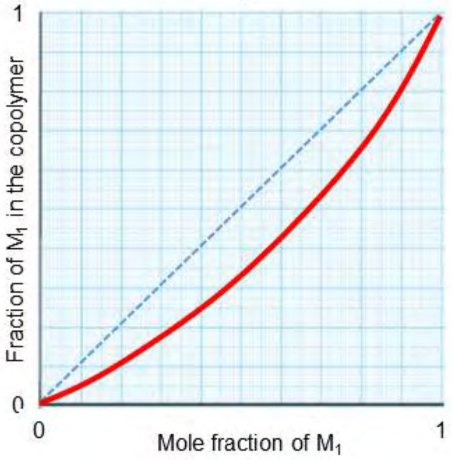
D



E

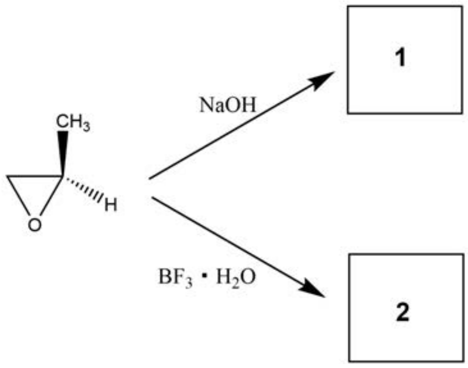


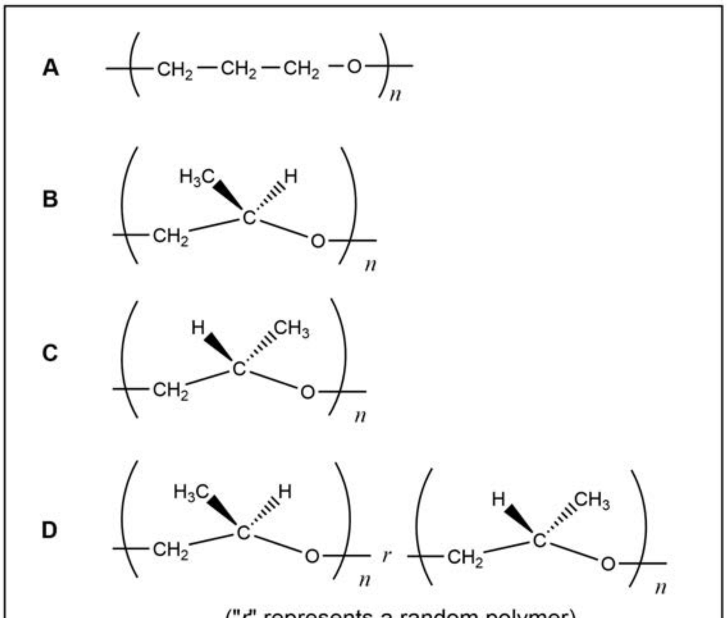
F



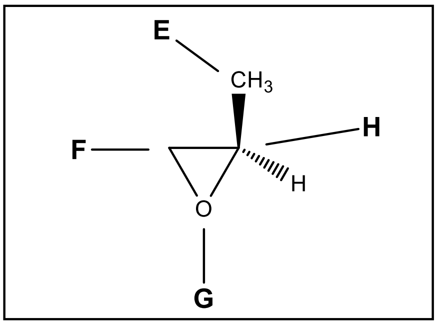
5. A copolymer that contains two types of monomers (M_1 and M_2) with a monomer reactivity ratio of $r_1 = 0.40$ and $r_2 = 0.10$ is synthesized using a radical polymerization initiator. In order to synthesize a copolymer with an M_1 content of 50 mol% at the initial stage of polymerization, **<u>how much</u>** M_1 must be mixed with M_2? Your answer should be expressed in terms of mol% of M_1 relative to the two monomers.

6. The configuration of the obtained polymer is different when a) NaOH (anionic polymerization) or b) BF_3 in the presence of a small amount of water (cationic polymerization) is added as an initiator to optically active propylene oxide. Among (**A** – **D**), **<u>select</u>** the appropriate polymer structure for **1** and **2**. In addition, **<u>select</u>** among (**E** – **H**) the site where the initiator reacts during the synthesis of **1** and **2**.





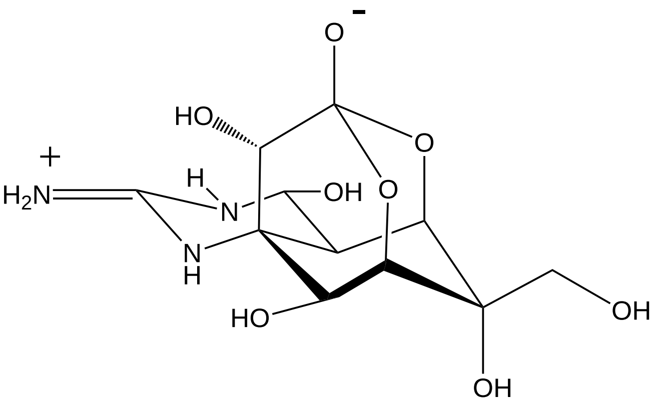
("*r*" represents a random polymer)



Problem 31. Total synthesis of tetrodotoxin

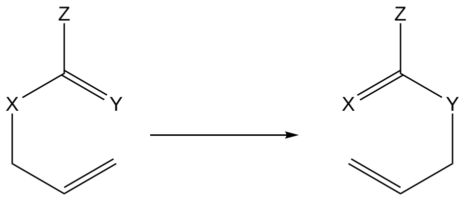
The ‘Fugu’ fish, which inflates and threatens when angry, has a delicious taste and is marketed as a delicacy in Japan.

However, fugu fish are also very dangerous as they contain highly toxic substances such as tetrodotoxin (**TTX**). The structure of **TTX** has been determined, and its asymmetric total synthesis has been accomplished.



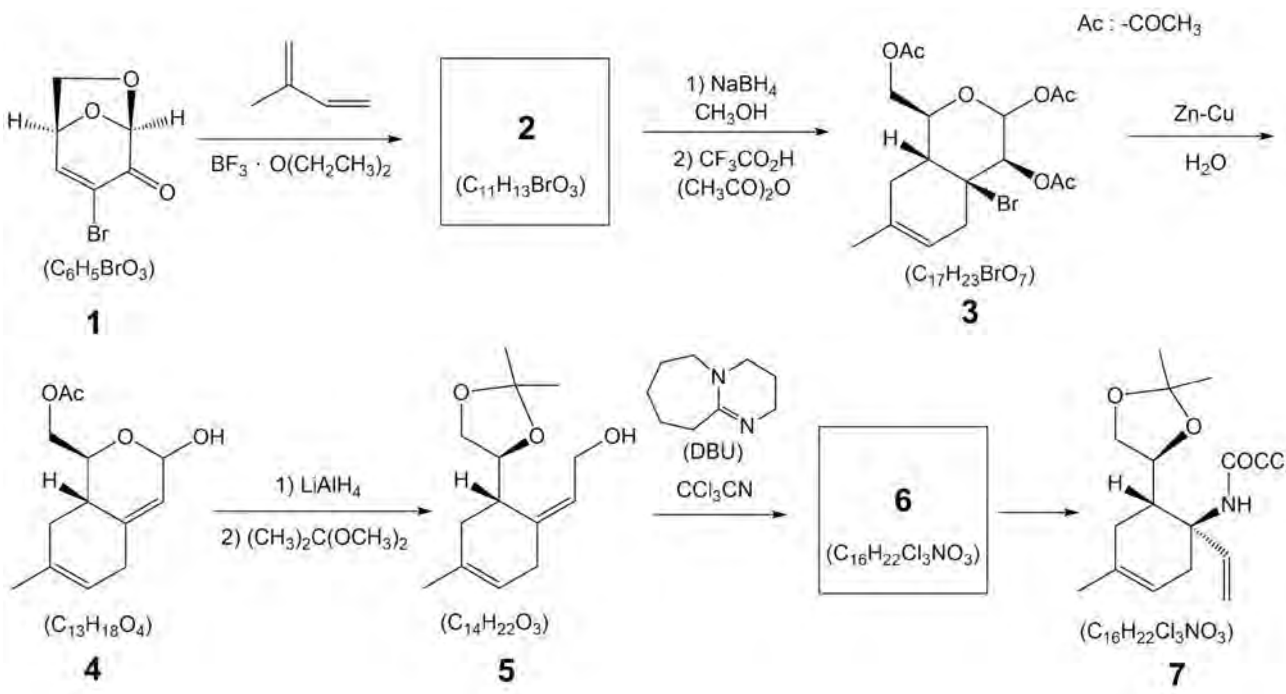
Tetrodotoxin (**TTX**)

1. Compound **7** was synthesized from **1** via the synthetic route shown below. **<u>Draw</u>** the structures of **2** and **6** and clearly identify the stereochemistry where necessary. Compound **7** is the product of [3,3]-sigmatropic rearrangement from a compound with 3-hetero-atomic-1,5-diene structure as shown in the following scheme.

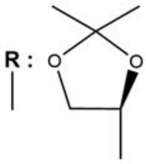


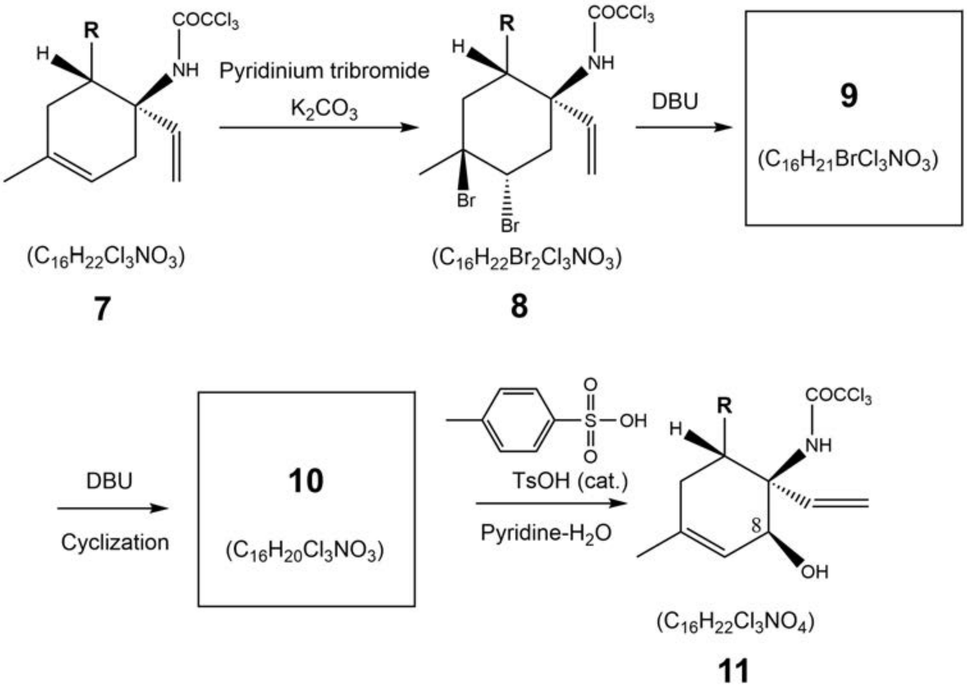
X = O, Y = NH

Scheme. [3,3]-Sigmatropic rearrangement reaction

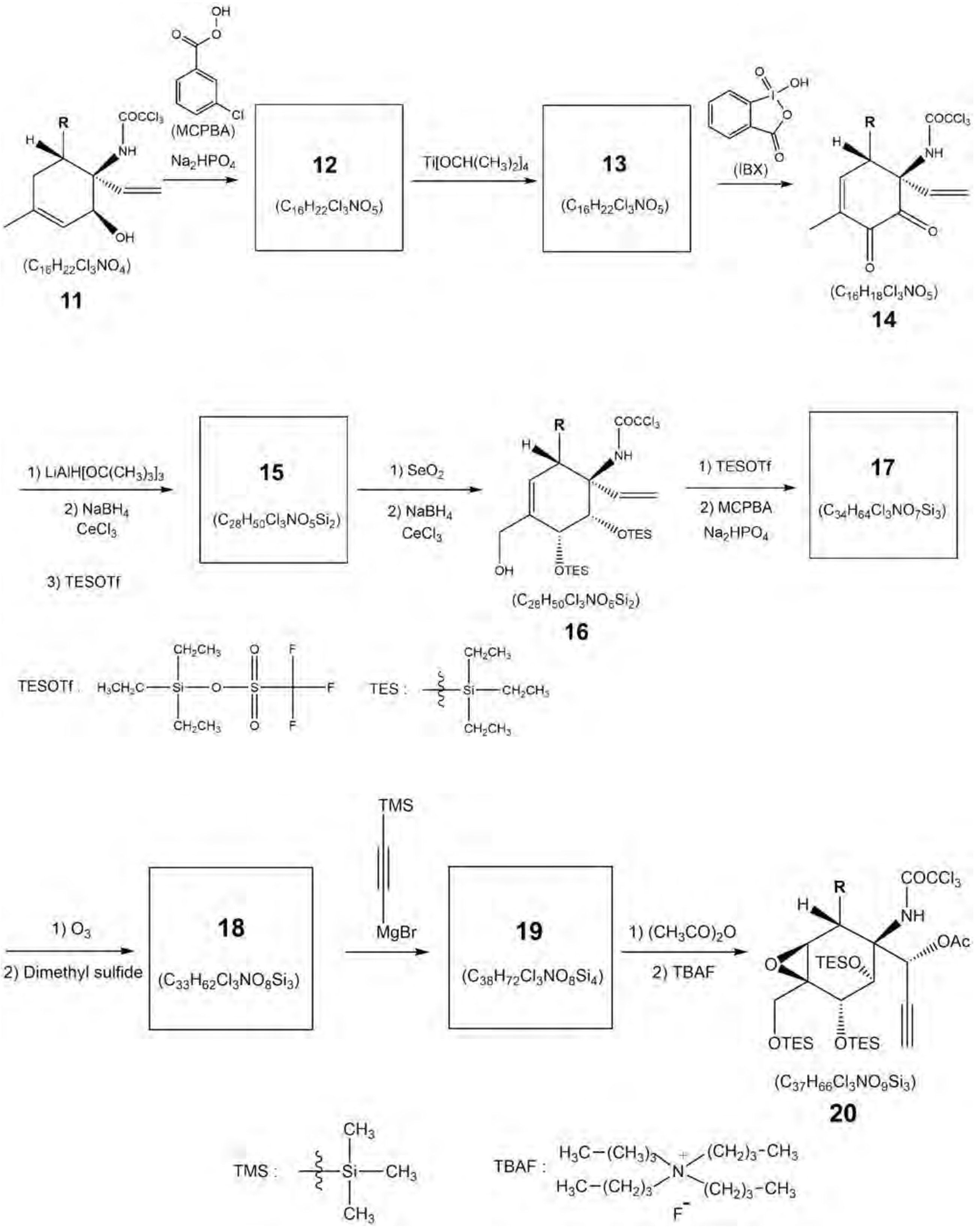


2. To synthesize **11**, a hydroxy group is introduced into **7** in a site-specific and stereoselective manner. **<u>Draw</u>** the structures of **9** and **10** and clearly identify the stereochemistry where necessary.

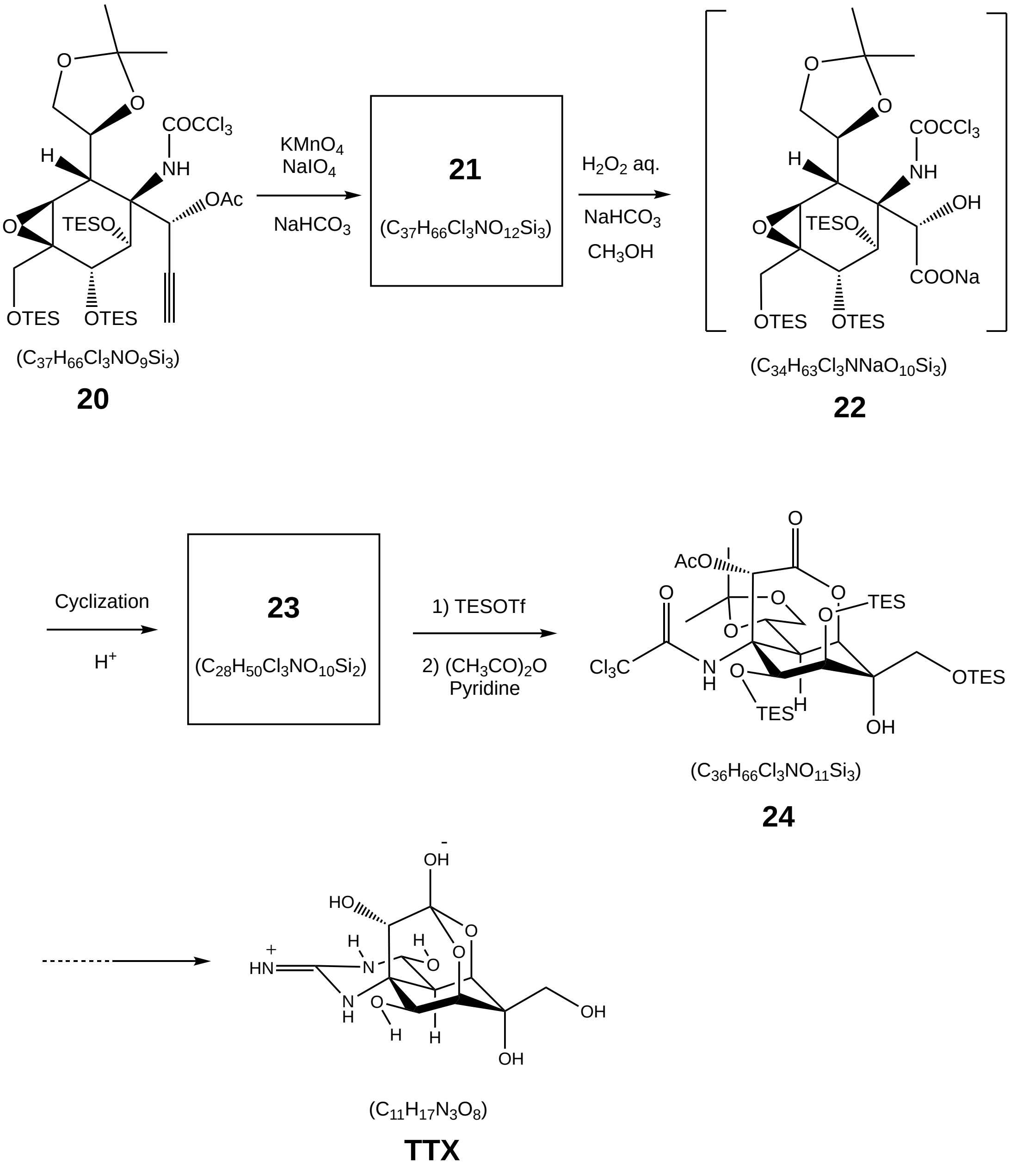




3. More hydroxy groups and oxygen-based functional groups required for the synthesis of **TTX** are introduced by epoxidation of the ring olefin, isomerization to an allyl alcohol, oxidation of the allylic position with SeO_2, and another epoxidation. **Draw** the structures of **12**, **13**, **15**, **17**-**19** in the reaction scheme below and clearly identify the stereochemistry where necessary.



4. During the synthesis of **24** from **20**, a regioselective ring opening of epoxide is carried out in the conversion from **22** to **23**. The total synthesis of **TTX** was achieved by hydrolyzing all protecting groups under acidic conditions after the introduction of guanidine. The total synthesis of TTX was achieved by hydrolyzing all protecting groups under acidic conditions after the introduction of guanidine. **Draw** the structures of alpha-keto acid derivative **21** and cyclization product **23** and clearly identify the stereochemistry where necessary.



Appendix

Practical Tasks

Task 1. Analysis of the saponification rate using a pH meter

Purpose

Although the hydrolysis of esters is very slow in itself, it is significantly accelerated by the presence of acids or bases, which act as catalysts. A typical ester hydrolysis reaction is the saponification of fats and oils, which produces soap. In the saponification reaction using sodium hydroxide, hydroxide ions are consumed because the organic acids produced react with sodium hydroxide. In the saponification of ethyl acetate using sodium hydroxide, the reaction rate, *v*, is proportional to the product of the concentration of ethyl acetate, $[\mathrm{CH_3COOC_2H_5}]$, and the concentration of hydroxide ions, $[\mathrm{OH^-}]$, according to:

$$v = k_2[\mathrm{CH_3COOC_2H_5}]\,[\mathrm{OH^-}]$$

where k_2 is the rate constant of the second-order reaction.

When ethyl acetate is present in excess relative to sodium hydroxide, the concentration of ethyl acetate can be considered constant during the reaction. The reaction under such conditions is known as a pseudo-first-order reaction. By defining the reaction rate constant k_1' as:

$$k_1' = k_2[\mathrm{CH_3COOC_2H_5}],$$

the reaction rate, *v*, can be expressed as:

$$v = k_1'\,[\mathrm{OH^-}]$$

Therefore, the reaction rate constants k_1' and k_2 can be obtained by examining the change in the hydroxide ion concentration over time. In this experiment, the concentration of the hydroxide ion during the saponification of ethyl acetate is monitored using a pH meter, and the reaction rate constant is determined by analyzing the results.

Chemicals

Substance	**Name**	**State**	**GHS Codes**
$C_4H_8O_2$	Ethyl acetate	liquid	H225, H320, H332, H335, H336
NaOH	Sodium hydroxide aqueous solution	liquid	H315, H318, H371
$C_6H_4(COOH)(COOK)$	Potassium hydrogen phthalate aqueous solution (pH = 4 standard solution)	liquid	Not applicable
KH_2PO_4	Potassium dihydrogen phosphate aqueous solution (pH = 7 standard solution)	liquid	H320
Na_2HPO_4	Disodium hydrogen phosphate aqueous solution (pH = 7 standard solution)	liquid	H320
$Na_2B_4O_7 \cdot 10H_2O$*	Sodium tetraborate aqueous solution (pH = 9 standard solution)	liquid	H360
$NaHCO_3$	Sodium hydrogen carbonate aqueous solution (pH = 10 standard solution)	liquid	Not applicable
Na_2CO_3	Sodium carbonate aqueous solution (pH = 10 standard solution)	liquid	H318, H332, H335, H336

*If students use the pH = 9 standard solution, it should be prepared by the mentor. Otherwise, a pH = 10 standard solution should be used.

Glassware and equipment

Volumetric flasks (2 pcs; 100 mL), Erlenmeyer flask with stopper (2 pcs), volumetric pipette (2 pcs; 25 mL), volumetric pipette (1 pc; 2 mL), pipette (1 pc), stir bar (1 pc), stopwatch (1 unit), pH meter (1 unit), water bath (1 unit), thermometer (1 unit), stirrer (1 unit), precision electronic balance (1 unit) [measurement accuracy: 0.1 mg].

Experimental procedure

Preparation of an aqueous solution of ethyl acetate

1. **Add** ion-exchanged water (ca. 50 mL) to a volumetric flask (100 mL) and weigh it on the precision electronic balance.
2. **Add** approximately 90 mg of ethyl acetate to the ion-exchanged water in the volumetric flask, and immediately close the flask with a stopper.
3. **Record** the mass of ethyl acetate based on the mass increase.
4. **Add** ion-exchanged water to the marked line to increase the volume to 100 mL and mix it.
5. Using a volumetric pipette, **transfer** 25 mL of the aqueous solution of ethyl acetate into an Erlenmeyer flask. **Place** the stir bar, **close** the flask with a stopper, and **place** it in a water bath at 30 °C to keep the temperature of the liquid constant.

Preparation of an aqueous solution of NaOH

1. **Add** ion-exchanged water (ca. 50 mL) to a volumetric flask (100 mL).
2. Using a volumetric pipette, **transfer** 2 mL of a 0.05 mol L^{-1} aqueous solution of NaOH to the volumetric flask, and then **add** ion-exchanged water to the marked line to increase the volume to 100 mL.
3. Using a volumetric pipette, **transfer** 25 mL of the aqueous solution of NaOH into an Erlenmeyer flask, **close** it with a stopper, and **place** the flask in a water bath at 30 °C to keep the temperature of the liquid constant.

Calibration of the pH meter

Calibrate the pH meter using three different pH standard solutions.

Saponification

1. **Begin** stirring the aqueous solution of ethyl acetate in the Erlenmeyer flask in the water bath.
2. Quickly **add** the aqueous solution of NaOH (25 mL), close the flask with a stopper and **start** timing with a stopwatch.
3. After 3 minutes, **insert** the thermometer and the electrodes of the pH meter.
4. **Measure** the temperature and the pH value of the solution every 5 minutes for 60 minutes.

Discussion

Relationship between the pH value and the reaction rate

The transformation and definite integration of $v = -\frac{\mathrm{d}[\mathrm{OH}^-]}{\mathrm{d}t} = k_1'[\mathrm{OH}^-]$ from $t = 0$ to $t = t$ gives:

$$-\ln\frac{[\mathrm{OH}^-]}{[\mathrm{OH}^-]_0} = k_1't$$

where $[\mathrm{OH}^-]_0$ is the initial concentration of sodium hydroxide, and $[\mathrm{OH}^-]$ is the concentration of sodium hydroxide at time t. Using the common logarithm, the equation will be:

$$-\log\frac{[\mathrm{OH}^-]}{[\mathrm{OH}^-]_0} = \frac{1}{2.303} \times k_1't.$$

Furthermore, this equation can be transformed to give:

$$-\log[\mathrm{OH}^-] + \log[\mathrm{OH}^-]_0 = \frac{1}{2.303} \times k_1't \qquad \text{(a)}$$

Since $[\mathrm{OH}^-] = \mathrm{pH} - 13.833$ at 30 °C, equation (a) can be rewritten as:

$$(\mathrm{pH})_0 - \mathrm{pH} = \frac{k_1'}{2.303} \times t$$

or:

$$\mathrm{pH} = -\frac{k_1'}{2.303} \times t + (\mathrm{pH})_0.$$

Here, $(\mathrm{pH})_0$ and pH are the pH value of the solution before the reaction and at time t, respectively.

Analysis

1. **Calculate** the concentration of the prepared aqueous solution of ethyl acetate (C_1) and the concentration of the diluted aqueous solution of NaOH (C_2).

C_1 [mol L^{-1}]	C_2 [mol L^{-1}]

2. **Write** the equation for the saponification of ethyl acetate with NaOH.

3. **Record** the temperature and the pH value of the solution.

Time (minutes)	Temperature (°C)	pH	Time (minutes)	Temperature (°C)	pH

4. **Plot** the time on the horizontal axis, the pH value on the vertical axis, and **determine** k_1' from the slope. Indicate the units.

5. **Determine** k_2. Given that the concentrations of the two aqueous solutions are low, it can be assumed that the volume after mixing is equal to the sum of the volumes of the two solutions.

6. The time when the concentration of the substrate is half of its initial concentration is called the half-life (time of half decay), which is represented using the symbol $t_{\frac{1}{2}}$. **Determine** $t_{\frac{1}{2}}$.

Task 2. Simultaneous acid–base titration

Introduction

Sodium carbonate, which is a raw material for glass, is produced by absorbing ammonia into an aqueous solution of sodium chloride and subsequent thermal decomposition of the sodium hydrogen carbonate obtained after passing carbon dioxide. Sodium carbonate can also be obtained by reacting carbon dioxide with an aqueous solution of sodium hydroxide, which is an important chemical for the production of soap, paper, and fibers.

In this experiment, a differential titration (Warder method) is used to simultaneously determine the concentrations of two electrolytes with different basicity. Specifically, the mass of the electrolytes in a mixed aqueous solution containing sodium hydroxide ($pK_a > 13$) and sodium carbonate ($pK_{a1} = 6.35$, $pK_{a2} = 10.33$) will be determined using two pH indicators.

Chemicals

Substance	**Name**	**State**	**GHS Codes**
HCl	Hydrochloric acid	Aqueous solution	H301, H314, H318, H330, H331, H334, H370, H372, H400
$C_{20}H_{14}O_4$	Phenolphthalein	Ethanol solution	H225, H320, H335, H336, H341, H351, H372, H373
$C_{14}H_{14}N_3NaO_3S$	Methyl orange	Aqueous solution	-
NaOH	Sodium hydroxide	Aqueous solution	H314, H318, H370, H402
Na_2CO_3	Sodium carbonate	Aqueous solution	H332, H318, H335, H336

Glassware and Equipment

- 1 Volumetric pipette, 20 mL with pipette filler
- 1 Burette, 25 mL
- 2 Erlenmeyer flasks with stopper (HCl standard solution, unknown alkali solution), 300 mL
- 1 Plastic container (for solution-state chemical waste), 1 L
- 2 Pipettes and pipetting bulbs (for indicators ***a*** and ***b***)
- 5 Titration flasks, 100 mL
- 1 Erlenmeyer flask (for transferring the HCl standard solution to the burette), 50 mL
- 1 Transfer funnel
- 1 Laboratory stand with burette clamp

Chemicals

- 0.1 mol L^{-1} HCl standard aqueous solution
- Unknown alkali solution containing NaOH and Na_2CO_3
- Indicator ***a***: Phenolphthalein ethanolic solution
- Indicator ***b***: Methyl orange aqueous solution
- Deionized water

Experimental procedure

(1) **Transfer** 20.00 mL of the unknown alkali aqueous solution into a 100 mL titration flask using a 20 mL volumetric pipette. **Add** indicator ***a***, which will turn the solution reddish purple. **Titrate** the unknown alkali solution by adding the HCl standard solution in the burette. When the alkali solution turns pale pink, you have reached the first equivalence point. **Record** the volume (V_a) in your notebook.

(2) **Add** indicator ***b*** to the now pale-pink aqueous solution. The color of the solution will turn yellow. **Continue** the titration using the HCl standard solution until the aqueous solution turns light orange, where you have reached the second equivalence point. **Record** the volume (V_b; volume from the first equivalence point to the second equivalence point).

Repeat procedures (1) and (2) if necessary.

Results

Titration Step (1)

No.	V_{final} (mL)	V_{initial} (mL)	V (mL)
1			
2			
3			
4			
5			
Accepted volume V_a			

Titration Step (2)

No.	V_{final} (mL)	V_{initial} (mL)	V (mL)
1			
2			
3			
4			
5			
Accepted volume V_b			

Questions

1. **Write** the two chemical equations for the neutralization reactions during titration step (1).

2. **Write** the chemical equation for the neutralization reaction during titration step (2).

3. From the results of the above titration operation, **calculate** the weights (g) of NaOH and Na_2CO_3 contained in 1 L of the unknown alkali aqueous solution.

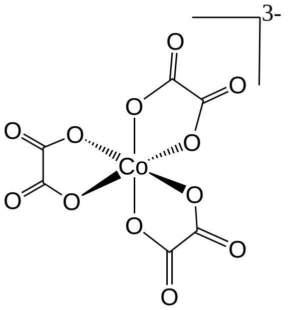
	Weight (g)
NaOH	
Na_2CO_3	

Calculation:

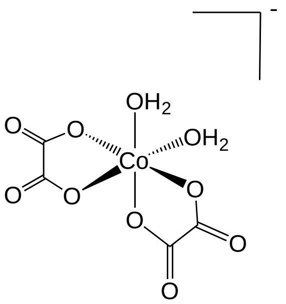
4. **Sketch** the pH titration curve expected for the unknown alkali solution.

Task 3. Synthesis and analysis of a cobalt(III) oxalate complex

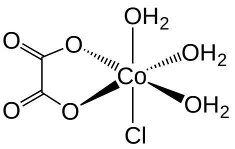
Cobalt is a silver-white ferromagnetic metal that belongs to the elements of the iron group. As it is less easily oxidized than iron as well as less corroded by acids and bases, alloys of cobalt with nickel, chromium, molybdenum, and other metals are used in equipment that requires wear resistance, such as cutting tools and high-grade materials such as scissors. Cobalt is also one of the trace biological essential elements because it is the central metal ion of vitamin B12. The most common oxidation states of cobalt are +2 and +3; cobalt ions in these oxidation states form metal complexes with a hexa-coordinated octahedral structure. In this problem, a cobalt(III) oxalate complex in which oxalate ions are coordinated to a cobalt ion is synthesized. Cobalt(II) chloride is oxidized with hydrogen peroxide and then treated with oxalic acid to obtain a green cobalt(III) oxalate complex. Below, three possible formulae for this complex are shown:



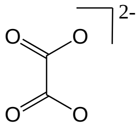
$K_3[Co(ox)_3]\bullet 3H_2O$



$K[Co(ox)_2(H_2O)_2]\bullet 3H_2O$



$[Co(ox)Cl(H_2O)_3]\bullet 3H_2O$



= oxalate (ox^{2-})

The number of oxalate ligands coordinated to the cobalt(III) oxalate complex synthesized in this experiment can be determined by titration with an aqueous potassium permanganate solution after decomposing the metal complex with an acid. The cobalt(III) oxalate complex is photosensitive and gradually decomposes from a green to a yellowish-brown product when exposed to visible or ultraviolet light. Thus, care must be taken when handling the sample in solution. In this experiment, this effect can be ignored if the measurement is performed immediately after the solution is prepared.

Chemicals

Substance	**Name**	**State**	**GHS Codes**
$[CoCl_2]\cdot 6H_2O$	Cobalt(II) chloride hexahydrate	Solid	H315, H319, H301, H334, H341, H351, H361, H335, H317
H_2SO_4 (aq), 6 M	Sulfuric acid	Aqueous solution	H314, H318, H330, H402, H370, H372
$K_2C_2O_4\cdot H_2O$	Potassium oxalate monohydrate	Solid	H301, H312
$Na_2C_2O_4$	Sodium oxalate	Solid	H319
H_2O_2 (aq), 30 %	Hydrogen peroxide solution	Aqueous solution	H272, H314, H318, H302, H312, H331, H351, H401, H370, H372
C_2H_5OH	Ethanol	Liquid	H225, H320
$KMnO_4$ (aq), ca. 0.02 M	Potassium permanganate	Aqueous solution	H272, H314, H318, H302, H341, H361, H335, H400, H410, H372
C	Activated carbon	Powder	NA

Glassware and equipment

- Erlenmeyer flask, 100 mL (2), 50 mL (1), 25 mL (3)
- Valves for Pasteur pipettes and rubber pipettes
- Hot plate
- Graduated cylinder, 25 mL
- Bath
- Ice bath
- Conical funnel and filter paper
- Glass filter for vacuum filtration
- Vacuum filtration set (Stand, flask-fixing clamp, aspirator, filtration flask or bottle, rubber adapter used for filtration)
- Burette (25 mL) and stand
- Small funnel to transfer the solution to the burette

Procedure

A. Synthesis of the cobalt(III) oxalate complex

1. **Add** 2.4 g of potassium oxalate monohydrate and 5 mL of water to a 100 mL Erlenmeyer flask, and **heat** the mixture to 70 °C in order to dissolve the solid.
2. In another 100 mL Erlenmeyer flask, **add** 1 g of cobalt(II) chloride hexahydrate followed by 3 mL of water to dissolve it. Then, **add** ca. 0.02 g of activated carbon powder followed by 1.0 mL of the 30% hydrogen peroxide solution.
3. **Add** the solution from step 1 to the solution from step 2 and **heat** the mixture while stirring in a water bath at 70 °C; the mixture will begin to foam. After further heating and stirring for about 15 minutes, the foaming will subside, and the red color of the solution will gradually turn to a dark green.
4. **Remove** the activated carbon via vacuum filtration and **wash** it with a small amount of water to obtain a dark green solution. **Transfer** the filtrate to a 50 mL Erlenmeyer flask.
5. **Add** 10 mL of ethanol to the filtrate. A green precipitate will form. To aid the precipitation, **cool** the flask in an ice bath for 0.5 h.
6. **Separate** the precipitate using vacuum filtration and **wash** it with a small amount of a water–ethanol (50/50, v/v) solution.
7. **Allow** the crystals **to air-dry** or **dry** them between two sheets of filter paper.
8. **Weigh** a clean empty vial (sample container) and **place** the dry crystals in the container to determine the weight of the resulting cobalt oxalate complex crystals.

B. Analysis of the cobalt oxalate complex

B-1.Standardization of the potassium permanganate aqueous solution (ca. 0.02 M)

Transfer the aqueous potassium permanganate solution (ca. 0.02 M) to a 25 mL burette. Accurately **weigh out** ca. 50 mg of sodium oxalate into a 100 mL Erlenmeyer flask, and then **add** 20 mL of water and 5 mL of 6 M sulfuric acid. **Warm** the flask in a hot water bath to approximately 80 °C. **Titrate** this oxalate solution with the aqueous potassium permanganate solution. When the mixture turns light pink and the color is maintained for about 1 minute, the end point of the titration has been reached. **Record** the amount of potassium permanganate aqueous solution required for the titration and **determine** its molar concentration.

B-2. Analysis of the cobalt oxalate complex

1. Accurately **weigh out** ca. 20 mg of the cobalt oxalate complex synthesized in A and **place** it in a 100 mL Erlenmeyer flask. To this Erlenmeyer flask, **add** 20 mL of water and 5 mL of 6 M sulfuric acid. **Warm** the mixed solution in the Erlenmeyer flask in a hot water bath maintained at ca. 80 °C.
2. **Titrate** the solution in the warm Erlenmeyer flask with the aqueous solution of potassium permanganate standardized in B-1. The end point is determined in the same way as above. **Record** the amount of the aqueous potassium permanganate solution required for the titration.

Questions

1. **Write** the values of the following data obtained in the experiment.

1-1. Weight of the crystals of the complex obtained in A. ____________________g

1-2 Weight of sodium oxalate used in B-1. ____________________g

1-3 Volume of the aqueous potassium permanganate solution (accepted) used in the titration in B-1.

____________________mL

1-4 Concentration of the aqueous potassium permanganate solution in B-1.

____________________mol L^{-1}

1-5 Weight of cobalt oxalate complex analyzed in B-2. ____________________g

1-6 Volume of the potassium permanganate aqueous solution (accepted) used in the titration in B-2.

____________________mL

2. **Write** the chemical equation of the reaction used in B-1.

3. **Find** the ratio (% by weight) of the oxalate ion relative to the cobalt oxalate complex. Then, assuming that the synthesized cobalt oxalate complex has one of the following compositions, **determine** the composition ratio of the cobalt ion to the oxalate ligand.

   - tris complex: $K_3[Co(C_2O_4)_3]\cdot 3H_2O$
   - bis complex: $K[Co(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$
   - mono complex: $[Co(C_2O_4)Cl(H_2O)_3]\cdot 3H_2O$

Weight% of oxalate ion ____________________%

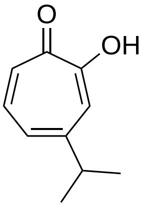
Cobalt ion to oxalate ligand composition ratio _______:_______

4. **Calculate** the yield of the complex based on the raw cobalt material.

Yield of complex ____________________%

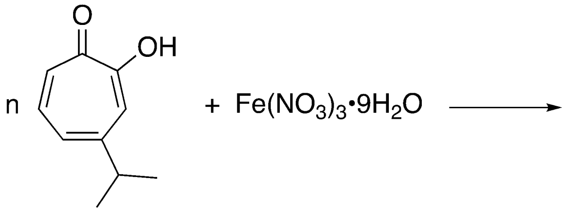
Task 4. Hinokitine: synthesis of a deep-red-colored natural product

Non-benzenoid aromatic compounds based on seven-membered ring systems have been widely investigated for many years both with respect to fundamental and applied chemistry. One such compound, 4-isopropyltropolone, is known as 'hinokitiol', as it had originally been isolated from an essential oil of the *Chamaecyparis obtuse* var. *formosana* (*Taiwan Hinoki*) tree. Hinokitiol is used in *e.g.* cosmetics, sunscreens, and oral care products. Recently, it has also been reported that hinokitiol can restore iron transport into, within, and/or out of cells, and thus may have potential in treating some genetic diseases.



Hinokitiol

The iron complex of hinokitiol, which is known as 'hinokitine', is found in the heartwood of *Taiwan Hinoki*, *Thuja dolabrata*, and *Thujopsis dolabrata*. In this task, you will synthesize hinokitine starting from hinokitiol and iron(III) nitrate nonahydrate.



<u>Chemicals</u>

Substance	**Name**	**State**	**GHS Codes**
$C_{10}H_{12}O_2$	Hinokitiol	Solid	H302, H361
$Fe(NO_3)_3 \cdot 9H_2O$	Iron(III) nitrate nonahydrate	Solid	H272, H315, H319, H402, H412
C_2H_5OH	Ethanol	Liquid	H225, H320
$CH_3COOC_2H_5$	Ethyl acetate	Liquid	H225, H320, H332, H335, H336
SiO_2	Silica gel	Solid	H351, H402
	Sea sand	Solid	

Glassware and equipment

- 2 Vials (20 mL)
- 1 Spatula
- 1 Weighing balance (0.001 g)
- 2 Weighing papers
- 1 Magnetic stirrer
- 1 Magnetic stir bar (small)
- 4 Pasteur pipettes
- 1 Filter funnel (small)
- 1 Filter paper
- 1 Filtering flask
- 1 Aspirator
- 1 Laboratory stand
- 1 Bosshead and clamp
- 1 Column tube with stopcock (inner diameter: 12 mm)
- 1 Beaker (100 mL)
- 2 Erlenmeyer flasks (100 mL)
- 2 Funnels
- Absorbent cotton
- 1 Glass rod
- 1 Eggplant flask
- 1 Rotary evaporator

Procedure

Synthesis of hinokitine

1. **Charge** a 20 mL vial (vial A) with hinokitiol (50 mg), iron(III) nitrate nonahydrate (25 mg), ethanol (0.8 mL), and a small magnetic stir bar.
2. Vigorously **stir** the reaction mixture at room temperature for 50 minutes.
3. **Collect** the product by vacuum filtration using a small filter funnel. **Transfer** all the contents of vial A to the filter funnel.
4. **Wash** the product with a small amount of ethanol using a Pasteur pipette.
5. **Let** the product **dry** on the filter funnel by continuing suction for more than 10 minutes.
6. **Transfer** the product to a 20 mL vial (vial B).

Purification of hinokitine by column chromatography on silica gel

Packing the silica gel column

1. Loosely **pack** a small plug of cotton at the bottom of the column tube using a glass rod.
2. **Clamp** the column tube to a laboratory stand. **Add** sea sand to fill the curved part of the column tube.
3. **Add** silica gel (5 g) and ethyl acetate (30 mL) as the eluent to a 100 mL beaker.
4. Carefully **pour** the silica gel slurry into the column tube using a funnel.
5. **Rinse** off any silica gel adhered to the side of the column tube with a small amount of the eluent.
6. **Tap** on the side of the column tube to help the silica gel to settle uniformly.

Loading the sample onto the column

7. **Dissolve** the product in vial B by adding a small amount of ethyl acetate.
8. **Open** the stopcock of the column tube and **reduce** the eluent level to the top of the silica gel. Be sure that the silica gel is always covered with the eluent.
9. **Close** the stopcock and **load** the solution in vial B onto the top of the silica gel using a Pasteur pipette.
10. **Open** the stopcock and **reduce** the solution level to the top of the silica gel.
11. **Close** the stopcock, **rinse** vial B with a small amount of the eluent and **load** the washings onto the top of silica gel using the Pasteur pipette.
12. **Open** the stopcock and **reduce** the solution level to the top of the silica gel.
13. **Repeat** steps 11 and 12 one or two more times.
14. **Close** the stopcock and **add** a small amount of the eluent to the column using a Pasteur pipette. **Open** the stopcock and **add** more eluent to the column.

Eluting and collecting the sample

15. **Collect** the colored fraction in a 100 mL Erlenmeyer flask. **Add** more eluent to the column if necessary.
16. **Weigh** a 100 mL eggplant flask and **record** the value.
17. **Transfer** the solution in the Erlenmeyer flask to the eggplant flask using a funnel.
18. **Evaporate** the solvent in the flask using a rotary evaporator.
19. **Submit** the flask for the evaluation.

Using the above procedures, hinokitine should be obtained as a deep red solid in more than 80% yield.

Questions

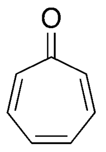
1. **Calculate** the theoretical yield of hinokitine.

2. **Write** the side product other than hinokitine.

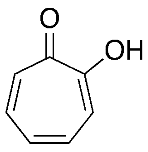
3. **Draw** the structures of hinokitine. **Explain** how many isomers, including enantiomers, are possible for hinokitine.

Task 5. Functionalization of a seven-membered ring: synthesis of tropolone tosylate

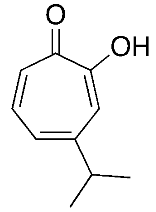
Tropolone is a derivative of tropone (cyclohepta-2,4,6-trienone) wherein a hydroxy group is bound to the carbon atom adjacent to the ketone group on the conjugated seven-membered ring. Tropone, tropolone, and their derivatives constitute an important class of organic cyclic compounds that have aromatic character due to the contribution of the tropylium ion structure with six π-electrons. The natural product hinokitiol (4-isopropyltropolone) is a typical tropolone-type compound derived from an essential oil of the *Hinoki* tree family, and shows effective antibacterial and antimicrobial properties.



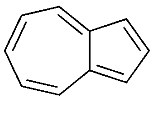
Tropone



Tropolone

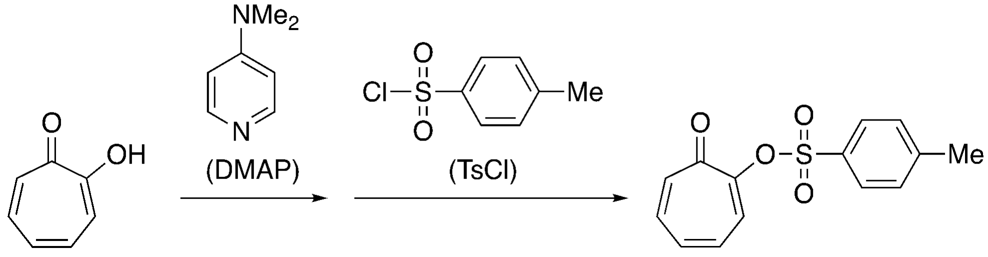


Hinokitiol



Azulene

In this task, you will synthesize tropolone tosylate by the reaction of tropolone with 4-dimethylaminopyridine (DMAP) followed by tosyl chloride (TsCl). Tropolone tosylate is commercially available and useful for the construction of fused ring systems such as ‘azulene’ compounds.



Chemicals

Substance	Name	State	GHS Codes
$C_7H_6O_2$	Tropolone	Solid	
$(CH_3)_2NC_5H_4N$	4-Dimethylamino-pyridine (DMAP)	Solid	H315, H319, H301, H371
C_2H_5OH	Ethanol	Liquid	H225, H320
$CH_3C_6H_4SO_2Cl$	Tosyl Chloride (TsCl)	Solid	H314, H315, H318

Glassware and equipment
- 2 Vials (20 mL)
- 1 Spatula
- 1 Weighing balance (0.001 g)
- 2 Weighing papers
- 1 Magnetic stirrer
- 1 Magnetic stir bar (small)
- 2 Pasteur pipettes
- 1 Filter funnel (small)
- 1 Filter paper
- 1 Filtering flask
- 1 Aspirator

Procedure: Synthesis of tropolone tosylate

1. **Charge** a 20 mL vial (vial A) with tropolone (125 mg), ethanol (1.0 mL), and a small magnetic stir bar.
2. Slowly **add** 4-dimethylaminopyridine (DMAP; 126 mg) to vial A while stirring the reaction mixture.
3. After the addition of DMAP, **stir** the reaction mixture at room temperature for another 10 minutes.
4. Slowly **add** tosyl chloride (TsCl; 196 mg) while stirring the reaction mixture.
5. After the addition of TsCl, **stir** the reaction mixture at room temperature for another 50 minutes.
6. **Collect** the product by vacuum filtration using a small filter funnel. **Transfer** all the contents of vial A to the filter funnel.
7. **Wash** the product with a small amount of ethanol using a Pasteur pipette.
8. **Let** the product **dry** on the filter funnel by continuing suction for more than 10 minutes.
9. **Weigh** a 20 mL vial (vial B) and **record** the value.
10. **Transfer** the product to vial B for submission.

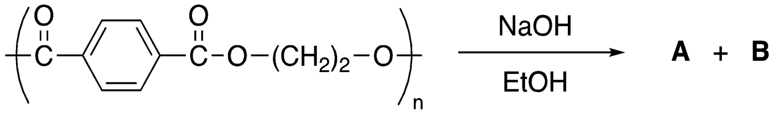
Using the above procedures, almost pure tropolone tosylate should be obtained as a light-brown solid in about 30% yield, which can be confirmed by ^{1}H NMR spectroscopy.

Questions

1. **Draw** the structure of the reaction intermediate resulting from the reaction between tropolone and 4-dimethylaminopyridine (DMAP). **Explain** the role of DMAP in this reaction.
2. **Describe** a procedure for the recovery of DMAP after the tosylation of tropolone.
3. What tosylation product(s) would be obtained from the above reaction if hinokitiol was used instead of tropolone? **Draw** the structure(s) of the tosylation product(s) of hinokitiol.

Task 6. Hydrolysis of polyethylene terephthalate: A small experiment for us, but a giant leap toward a more sustainable society

Poly(ethylene terephthalate) (PET), the raw material for PET bottles, is one of the most common plastics. In recent years, growing concern about the environmental impact of plastic waste has prompted the development of efficient technologies to recycle plastics. Chemical recycling, which is based on decomposing plastic into its raw monomer materials and reusing the recycled monomers for the production of new plastics, is an important technology because it allows the production of recycled plastics with high purity. This task explores the chemical recycling of plastics through an experiment involving the hydrolysis of PET.



Materials
- A strip of PET cut from a PET bottle, 1.00 g
- Sodium hydroxide, 3.0 g
- Ethanol, 50 mL

Substance	Name	State	GHS Codes
$(C_{10}H_8O_4)_n$	Poly(ethylene terephthalate)	Solid	-
NaOH	Sodium Hydroxide	Solid	H314, H318, H370
C_2H_6O	Ethanol	Liquid	H225, H320

Glassware and equipment
- Laboratory stand with clamps
- Magnetic stirrer and a stir bar
- Oil bath with a temperature controller
- Round-bottom flask (100 mL): A wide-mouthed flask is preferred.
- Round-bottom flask (20 mL)
- Reflux condenser and rubber tubes for supplying water as the coolant
- Graduated cylinder (100 mL)
- Beaker (100 mL)
- Buchner funnel and filter paper
- Vacuum flask (100 mL) and rubber adapter to connect the Buchner funnel
- Aspirator for vacuum filtration. An alternative such as a dry pump can be used.
- Pipette (10 mL)
- Petri dish
- Tweezers to handle the PET strip
- Weighing balance

Experimental procedure

Hydrolysis of PET

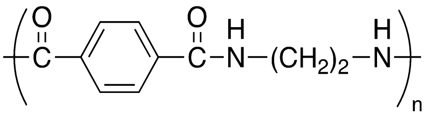
1. **Heat** the oil bath to 100 °C.
2. **Add** 5.0 g of sodium hydroxide and 30 mL of ethanolic to a 100 mL round-bottom flask in order to prepare an ethanol solution of sodium hydroxide.
3. **Weigh** a strip of PET and **place** it in the flask.
4. **Connect** the reflux condenser to the flask and run water. **Immerse** the bottom of the flask in the oil bath to start heating and refluxing. After 30 minutes, **lift** the flask from the oil bath.
5. **Remove** the residual PET from the flask using tweezers and **wash** it with a small amount of ethanol. **Place** the PET strip on a filter paper, **dry** it under air, and then **weigh** it.
6. **Filter** the suspension remaining in the flask using vacuum filtration. **Wash** the solid on the filter paper with a small amount of ethanol and **dry** it by continuing suction to obtain crude crystals of compound **A** shown in the reaction scheme.
7. **Transfer** the crude crystals of **A** on the filter paper to a petri dish and **weigh** them.

Recrystallization of **A**

1. **Place** the crude crystals of **A** in a 20 mL round-bottom flask and **add** 2 mL of water. **Dissolve** the crude crystals by heating the mixture to 100 °C using an oil bath. If necessary, **add** 0.5 mL of water to dissolve all the crude crystals.
2. **Allow** the solution **to cool** to room temperature. **Collect** the precipitated crystals of **A** via vacuum filtration, **wash** them with a small amount of ethanol and **dry** them with continuing suction.
3. **Transfer** the crystals of **A** to a petri dish and **weigh** them.

Questions

1. **Draw** the structural formulas of **A** and **B**.
2. **Calculate** the yield of **A** based on the amount of PET used.
3. **Calculate** the yield of **A** based on the amount of PET reacted.
4. **Draw** a reaction mechanism for the cleavage of ester bonds in the reaction of PET and NaOH.
5. This reaction is irreversible. **Describe** the reasons for this.
6. **Which would be more efficient**: The hydrolysis of PET conducted in this experiment or the hydrolysis of the polyamide shown below under the same conditions? The reasons for your answer should be also described.



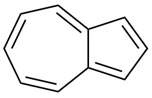
Task 7. Separation of blue and red components from a green mixture

In 1903, Tswett reported the first example of chromatography: Leaves were ground and developed on filter paper to separate pigments such as chlorophyll, carotenes, and xanthophylls. The term chromatography is derived from the Greek *chroma*, which means ‘color’, and *graphein*, which means ‘to write’. While chromatography was initially applied to colored compounds, nowadays, it is also applied to colorless compounds.

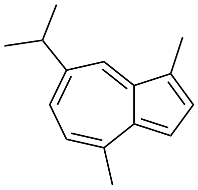
Chromatography is a very powerful method to separate the individual constituents of compound mixtures. In this task, chromatography is compared to recrystallization, which is another popular separation/purification method.

For that purpose, we will use a mixture of guaiazulene and 4-(phenylazo)phenol (henceforth denoted as the ‘mixture’) in this task. Guaiazulene is a natural pigment that is found in some essential oils. Given the special electronic structure of the azulene skeleton (*vide infra*), guaiazulene exhibits a deep blue color, which stands in stark contrast to other isomeric naphthalene derivatives. The second component of our mixture, 4-(phenylazo)phenol, is a product of one of the simplest diazo coupling reactions. Conjugated azo compounds represent an important class of chromophores, and various azo dyes have found applications in *e.g.* the textile and food industry.

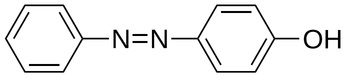
In this task, considering the historic origins of ‘chromatography’, we will separate the two individual colored compounds from the ‘mixture’.



azulene



guaiazulene



4-(phenylazo)phenol

Chemicals

Substance	Name	State	GHS Codes
$C_{15}H_{18}$	Guaiazulene	Solid	H302
$C_6H_5N{=}NC_6H_4OH$	4-(Phenylazo)phenol	Solid	H302, H315, H319
C_2H_5OH	Ethanol	Liquid	H225, H320
C_6H_{14}	Hexane	Liquid	H225, H315, H319, H361, H335 H336, H304, H401, H372
$CH_3COOC_2H_5$	Ethyl acetate	Liquid	H225, H320, H332, H335, H336
SiO_2	Silica gel	Solid	H351, H402
	Sea sand	Solid	

Samples

A ‘mixture’ for the recrystallization; ca. 1:5 (w/w) mixture of guaiazulene and 4-(phenylazo)phenol.

A ‘mixture’ for the column chromatography; ca. 1:1 (w/w) mixture of guaiazulene and 4-(phenylazo)-phenol.

Solutions

A solution for the recrystallization; 1:1 (v/v) mixture of ethanol and hexane.

A solution to charge the sample; 1:1 (v/v) mixture of hexane and ethyl acetate.

Second eluent; 4:1 (v/v) mixture of hexane and ethyl acetate.

Glassware and equipment

- 2 Short test tubes
- 1 Test tube rack
- 5 Pasteur pipettes
- 3 Spatulas
- 1 Weighing balance (accuracy: 0.001 g)
- 1 Hot water bath
- 1 Ice bath
- 1 Graduated cylinder (50 mL)
- 1 Graduated cylinder (5 mL)
- 1 Filter funnel (small)
- 1 Filter paper
- 1 Filtering flask
- 1 Aspirator
- 1 Petri dish
- 1 Laboratory stand
- 1 Clamp
- 1 Glass column with stopcock (inner diameter: 12 mm)
- 1 Vial tube (4 mL)
- 4 Erlenmeyer flasks (100 mL)
- 1 Erlenmeyer flask (50 mL)
- 3 Funnels
- Cotton wool
- 1 Glass rod
- 2 Round-bottom flasks (100 mL)
- 1 Rotary evaporator

Procedure

Recrystallization of the 'mixture'

1. **Weigh** out a test tube and **place** ca. 0.5 g of the 'mixture' for the recrystallization into it; **weigh** the test tube again.
2. **Heat** the water bath to 80 °C.
3. **Add** 1.0 mL of the 1:1 (v/v) mixture of ethanol and hexane to the test tube. **Clamp** the test tube and **heat** it in the water bath until all of the 'mixture' has dissolved.
4. **Allow** the green solution **to cool** to room temperature. After crystals have formed, further **cool** the test tube with iced water.
5. **Place** the filter funnel on the filtering flask and **insert** the filter paper. **Connect** the filtering flask to the aspirator and **start** the suction. **Wet** the filter paper with a small amount of ethanol and press it to the filter funnel using a spatula.
6. **Add** the 1:1 mixture of ethanol and hexane to another test tube and **cool** it with iced water.
7. **Transfer** all of the precipitate onto the filter funnel with the cold ethanol-hexane mixture. **Wash** the crystals with a small amount of the cold ethanol-hexane mixture and **dry** them using continued suction.
8. **Weigh** the empty petri dish and **transfer** the product to the petri dish; **weigh** the petri dish again.

Separation of the ‘mixture’ by column chromatography on silica gel

Packing the silica gel column

1. Use a glass rod to loosely **insert** a small plug of cotton wool into the small glass tube just before the stopcock inside the column.
2. **Clamp** the column onto a laboratory stand. **Add** sea sand to fill the curved part on the bottom of the column.
3. **Place** silica gel (20 g) in an Erlenmeyer flask (50 mL), **add** hexane (30 mL) as the eluent, and **stir** the mixture to make a slurry.
4. Carefully **pour** the slurry into the column using a funnel.
5. **Rinse** off any silica gel adhered to the side of the column with a small amount of hexane.
6. Use something soft to gently **tap** on the side of the column to help the silica gel to settle uniformly.

Loading the sample onto the column

7. **Place** ca. 0.2 g of the ‘mixture’ for the column chromatography in a vial tube and **weigh** it. **Dissolve** the ‘mixture’ by adding a small amount of the 1:1 (v/v) mixture of hexane and ethyl acetate.
8. **Place** an Erlenmeyer flask under the column. **Open** the stopcock of the column and **lower** the eluent level to reach the top of the silica gel. Be sure that the silica gel is always covered by the eluent.
9. **Close** the stopcock and gently **load** the green solution in the vial onto the top of the silica gel using a Pasteur pipette.
10. **Open** the stopcock and **lower** the solvent level to reach the top of the silica gel.
11. **Close** the stopcock, **rinse** the vial with a small amount of the 1:1 hexane-ethyl acetate mixture, and **add** the washings onto the top of silica gel using the Pasteur pipette.
12. **Open** the stopcock and **lower** the solvent level to reach the top of the silica gel.
13. **Repeat** steps 11 and 12 one or two more times.
14. **Close** the stopcock, **place** sea sand on top of the silica gel, and **add** hexane to the column.

Eluting and collecting the sample

15. **Open** the stopcock; after collecting the first colorless fraction, **change** to the next Erlenmeyer flask to collect the first colored fraction. **Add** more hexane to the column if necessary.
16. After collecting the first colored fraction, **change** the Erlenmeyer flask to collect the subsequent colorless eluate. **Add** the 4:1 (v/v) mixture of hexane and ethyl acetate as the second eluent to the column and **continue** collecting.
17. After collecting the colorless eluate, **change** the Erlenmeyer flask to collect the second colored fraction. **Add** more of the 4:1 hexane-ethyl acetate mixture to the column if necessary. After collecting the second colored eluate, **close** the stopcock.
18. **Weigh** the empty round-bottom flasks.
19. **Transfer** each colored fraction from the Erlenmeyer flasks to individual round-bottom flasks using a funnel (use a clean funnel for each fraction).
20. **Remove** the solvent(s) from each flask using a rotary evaporator.
21. **Submit** the flask for evaluation.

Questions

1. **Name** the constituent obtained from recrystallization.
2. **Name** the constituent in each colored fraction obtained from column chromatography.
3. **Explain** why the recovery from recrystallization is almost never quantitative.
4. Chromatography is based on the interaction of the eluite (eluted molecules) with the stationary phase (in this case: Silica gel). **Which molecule engages** in stronger interactions with silica gel, guaiazulene or 4-(phenylazo)phenol? **Name** the functional group and the type of interaction that characterizes the affinity.

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