

42nd International Chemistry Olympiad Japan, 2010

Theoretical Problems



Chemistry : the key to our future



Instructions

- Ensure that your name and student code are written in the spaces provided at the top of each answer sheet.
- You have 5 hours to work on the problems.
- Use only the pen and the calculator provided.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded. Use the reverse of the sheets if you need scratch paper.
- Write any relevant calculations in the appropriate boxes when necessary. If you provide no working and only the correct result for a complicated calculation, you will receive no marks.
- Numerical answers are meaningless without the appropriate units. You will be heavily penalized if units are not given where required.
- You must stop work immediately when the STOP command is given. A delay in doing this may lead to your disqualification from the exam.
- When you have finished the examination, you must put your papers into the envelope provided, and seal the envelope by yourself.
- Do not leave your seat until permitted by the supervisors.
- This examination has 22 pages. The answer booklet comprises 17 pages.
- The official English version of this examination is available on request only for clarification.



Constants and Formulae

Avogadro constant:	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485 \text{ C mol}^{-1}$	$\Delta_r G^\circ = -RT \log_e K = -nFE_{\text{cell}}^\circ$	
Planck constant:	$h = 6.626 \times 10^{-34} \text{ J s}$	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \log_e \frac{c_{\text{ox}}}{c_{\text{red}}}$
Speed of light:	$c = 2.998 \times 10^8 \text{ m s}^{-1}$	Energy of a photon:	$E = \frac{hc}{\lambda} = h\nu$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log_{10} \frac{I_0}{I} = \varepsilon cl$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol L^{-1} . Consider all gases ideal throughout the exam.



Periodic table with relative atomic masses

1																	18
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc -	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -



Problem 1

8% of the total

1a	1b	1c	1d	1e	1f	1g	1h	1i	Task 1
2	4	2	1	1	1	3	2	1	17

In 1894, Lord Rayleigh reported that the mass of chemically prepared nitrogen was different from that of nitrogen extracted from the atmosphere, as shown in Tables 1 and 2. Later, this difference was attributed to the presence of argon in *atmospheric nitrogen*. The masses of gases were measured by using a glass vessel with a known volume under atmospheric pressure (1.013×10^5 Pa).

Table 1. Mass of *Chemical Nitrogen in the Vessel*

From nitric oxide	2.3001 g
From nitrous oxide	2.2990 g
From ammonium nitrite purified at a red heat	2.2987 g
From urea	2.2985 g
From ammonium nitrite purified in the cold	2.2987 g
Mean	2.2990 g

Table 2. Mass of *Atmospheric Nitrogen in the Vessel*

O ₂ was removed by hot copper (1892)	2.3103 g
O ₂ was removed by hot iron (1893)	2.3100 g
O ₂ was removed by ferrous hydrate (1894)	2.3102 g
Mean	2.3102 g

- a) Calculate the volume V [m³] of the vessel used by Rayleigh from the mean mass of *chemical nitrogen*, which must have been pure nitrogen. Assume that the measurements were carried out at a temperature of 15.0 °C.

The amount n of the pure nitrogen (*chemical nitrogen*), $M = 28.02$ g mol⁻¹, is

$$n = \frac{m}{M} = \frac{2.2990}{28.02} = 8.205 \times 10^{-2} \text{ mol.} \quad \text{[or equivalent]} \quad (1 \text{ pt})$$

Then, from the ideal gas law, $V = \frac{nRT}{p}$

$$= \frac{8.205 \cdot 10^{-2} \times 8.314 \times 288.15}{1.013 \cdot 10^5} = \underline{1.940 \times 10^{-3} \text{ m}^3}. \quad (1 \text{ pt})$$

$$V = \quad \text{m}^3$$

- b) Estimate the mole fraction x of argon in Rayleigh's *atmospheric nitrogen*, by assuming that argon and nitrogen were the only constituents. Use the mean masses of the *atmospheric* and *chemical nitrogen* for the calculation.

The equation for the ratio of the mass of *atmospheric* nitrogen to the mass of *chemical* nitrogen is

$$\frac{28.02(1-x) + 39.95x}{28.02} = \frac{2.3102}{2.2990} \quad \text{[or equivalent]} \quad (1 \text{ pt})$$

Transformation gives

$$x = \frac{(2.3102 - 2.2990) / 2.2990}{39.95 - 28.02} \times 28.02 \quad \text{[or equivalent]} \quad (2 \text{ pt})$$

$$= \underline{1.14 \times 10^{-2}} \quad (\text{or } 1.14\%) \quad (1 \text{ pt})$$

$x =$

Ramsay and Clève discovered helium in cleveite (a mineral consisting of uranium oxide and oxides of lead, thorium, and rare earths; an impure variety of uraninite) independently and virtually simultaneously in 1895. The gas extracted from the rock showed a unique spectroscopic line at around 588 nm (indicated by D₃ in Figure 1), which was first observed in the spectrum of solar prominence during a total eclipse in 1868, near the well-known D₁ and D₂ lines of sodium.

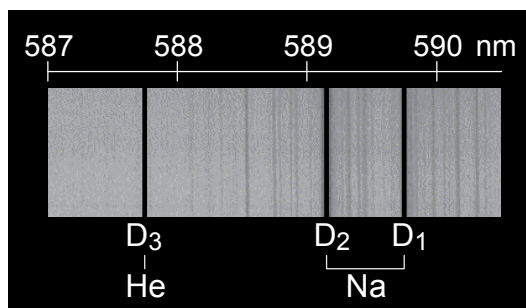


Figure 1. Spectral lines around 588 nm

- c) Calculate the energy E [J] of a photon with the wavelength of the D₃ line of helium shown in Figure 1.

According to Figure 1, the wavelength of the D₃ line is approximately 587.7 nm (no punishment if 587.8 or 588 is used).

The corresponding photon energy is $E = \frac{hc}{\lambda}$

$$= \frac{6.626 \cdot 10^{-34} \times 2.998 \cdot 10^8}{587.7 \cdot 10^{-9}} \quad (1 \text{ pt})$$

$$= \underline{3.380 \times 10^{-19} \text{ J}}. \quad (1 \text{ pt})$$

$E =$

J

Figure 2 shows an energy diagram of the atomic orbitals of helium. The arrows indicate the "allowed" transitions according to the spectroscopic principle.

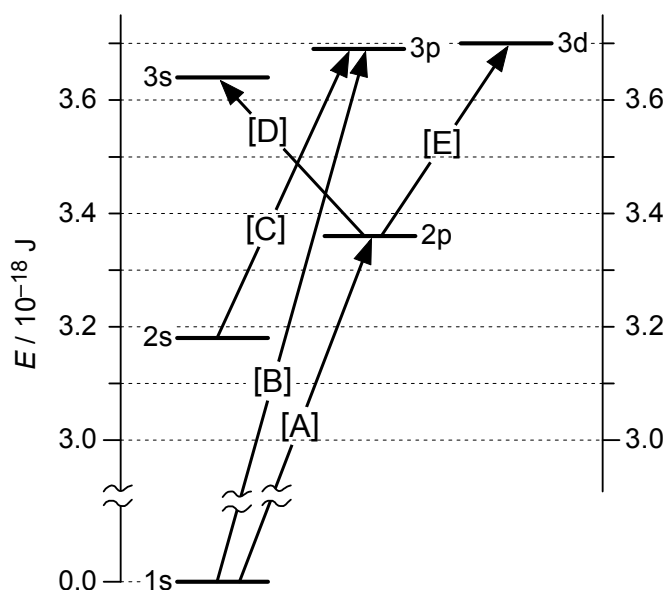
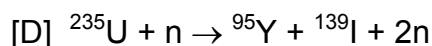
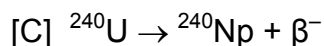
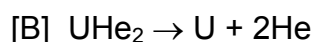
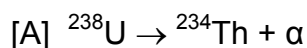


Figure 2. Energy diagram of atomic orbitals of helium when an electron resides in the 1s orbital.

- d) Identify the transition relevant to the D₃ line of helium among the transitions [A] to [E] indicated in Figure 2. Mark one on the answer sheet:

[E] The energy, 3.382×10^{-19} J, matches with the energy of the transition [E] between the 2p and 3d orbitals. (1 pt)
cf.) Energy difference [10^{-19} J] = [A]:33.6, [B]:36.9, [C]:5.1, [D]:2.8, [E]:3.4

- e) Which equation explains the occurrence of helium in cleveite among [A] to [D] below? Mark one on the answer sheet:

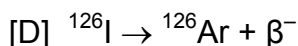
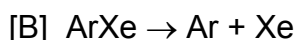
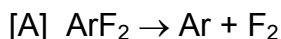


[A] Considering that the α particle is the nucleus of helium, α -decay [A] is the relevant source of helium in such rocks. No compound of He such as UHe_2 in [B] is known to be stable at ambient temperature. [C] is a radio active decay of ^{240}U in the thorium series. [D] is a nuclear fission reaction of ^{235}U occurring in nuclear reactors. The correct answer is [A]. (1 pt)



Argon is also found in minerals such as *malacon*.

- f) Which equation explains the occurrence of argon in rocks among [A] to [D] below? Mark one on the answer sheet.



[C] [C] is a well-known radioactive decay reaction occurring with a half-life of the order of the age of the earth. No stable compound of Ar, such as ArF_2 or ArXe , can be expected. Products of [D] should be $^{126}\text{Xe} + \beta^-$. The correct answer is [C]. (1 pt)

One of the strongest evidences for the monoatomicity of argon and helium is the ratio of the heat capacity under constant pressure to that at constant volume, $\gamma = C_p / C_V$, which is exactly 5/3 (1.67 ± 0.01) for a monoatomic gas. The ratio was derived from the measurement of speed of sound v_s by using the following equation, where f and λ are the frequency and wavelength of the sound, and R , T , and M denote the molar gas constant, absolute temperature, and molar mass, respectively.

$$v_s = f\lambda = \sqrt{\frac{\gamma RT}{M}}$$

For an unknown gas sample, the wavelength of the sound was measured to be $\lambda = 0.116$ m at a frequency of $f = 3520$ Hz ($\text{Hz} = \text{s}^{-1}$) and temperature of 15.0 °C and under atmospheric pressure (1.013×10^5 Pa). The density ρ of the gas for these conditions was measured to be 0.850 ± 0.005 kg m^{-3} .

- g) Calculate the molar mass M [kg mol^{-1}] of this gas.

The density ρ is given by $\rho = \frac{nM}{V}$. [or equivalent] (1 pt)

By combining with the ideal gas law gives:

$$M = \frac{\rho RT}{p} = \frac{0.850 \times 8.314 \times 288.15}{1.013 \cdot 10^5}$$
 [or equivalent] (1 pt)

$$= \underline{2.01 \times 10^{-2}} \text{ kg mol}^{-1}. (20.1 \text{ g mol}^{-1})$$
 (1 pt)

$M =$ kg mol⁻¹



h) Calculate the heat capacity ratio γ for this gas sample.

From the equation for the sonic velocity, $f\lambda = \sqrt{\frac{\gamma RT}{M}}$,

$$\gamma = \frac{M}{RT} (f\lambda)^2 = \frac{2.01 \cdot 10^{-2}}{8.314 \times 288.15} (3520 \times 0.116)^2 \quad [\text{or equivalent}] \quad (1 \text{ pt})$$

$$= \underline{1.40} \quad (1 \text{ pt})$$

$$(\text{or, using } \frac{M}{RT} = \frac{\rho}{p}, \gamma = \frac{\rho}{p} (f\lambda)^2 = \frac{0.850}{1.013 \cdot 10^5} (3520 \times 0.116)^2 = 1.40)$$

$$\gamma =$$

i) Which is this gas among [A] to [D]? Mark one on the answer sheet:

[A] HCl

[B] HF

[C] Ne

[D] Ar

[B] From $M = 20.1 \text{ g mol}^{-1}$, this gas must be HF or Ne.

From $\gamma = 1.4 (\neq 5/3 \approx 1.67)$, this is NOT a monoatomic gas (*i.e.*, HCl or HF).
Thus, this gas must be [B] HF. (1 pt)

Note: It is not possible to distinguish between HF ($M = 20.01$) and Ne ($M = 20.18$) from the molar mass only, which is 20.10 ± 0.12 by taking into account the uncertainty of $\rho (\pm 0.005 / 0.850 = \pm 0.6\%)$. However, the precision of $\gamma = 1.40$ is enough to exclude the possibility of monoatomic gas ($\gamma = 5/3 \approx 1.67$).



Problem 2

6% of the total

2a	2b	2c	2d	2e	Task 2
4	4	4	3	5	20

Crystal structure of alkali metal halide

In crystals of ionic compounds, cations are generally arranged in the interstices of the closest packed lattice of anions. The structure of an ionic crystal such as sodium chloride becomes stable when the cations are in contact with the nearest anions.

- a) In the crystal of sodium chloride, both Na^+ and Cl^- ions form a face-centered cubic lattice. Give the numbers of Na^+ and Cl^- ions in a unit cell and the coordination numbers of Na^+ and Cl^- ions in sodium chloride crystal.

Number of ions	Na^+ : 4	Cl^- : 4
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Coordination number	Na^+ : 6	Cl^- : 6
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[Total 4 pts]

[2 pt] Both number of Na^+ and Cl^- ions are correct.

[1 pt] Each coordination number of Na^+ and Cl^- ions is correct.

- b) The ionic radii of Na^+ and Cl^- ions in the crystal of sodium chloride are 0.102 nm and 0.181 nm, respectively. Calculate the density [kg m^{-3}] of the sodium chloride crystal.

[Total 4 pts]

Length of lattice l : $l = 0.102 \times 2 + 0.181 \times 2 = 0.566 \text{ nm}$ [2 pt]

Density ρ :

$$\rho = \frac{(22.99 + 35.45) \times 4}{(0.566 \times 10^{-9})^3 \times 6.022 \times 10^{23}} = 2.1408 \times 10^6 \text{ g m}^{-3} = 2.14 \times 10^3 \text{ kg m}^{-3}$$

[1 pt for the equation of density, 1 pt for final answer.]

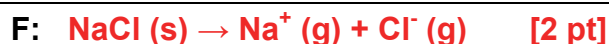
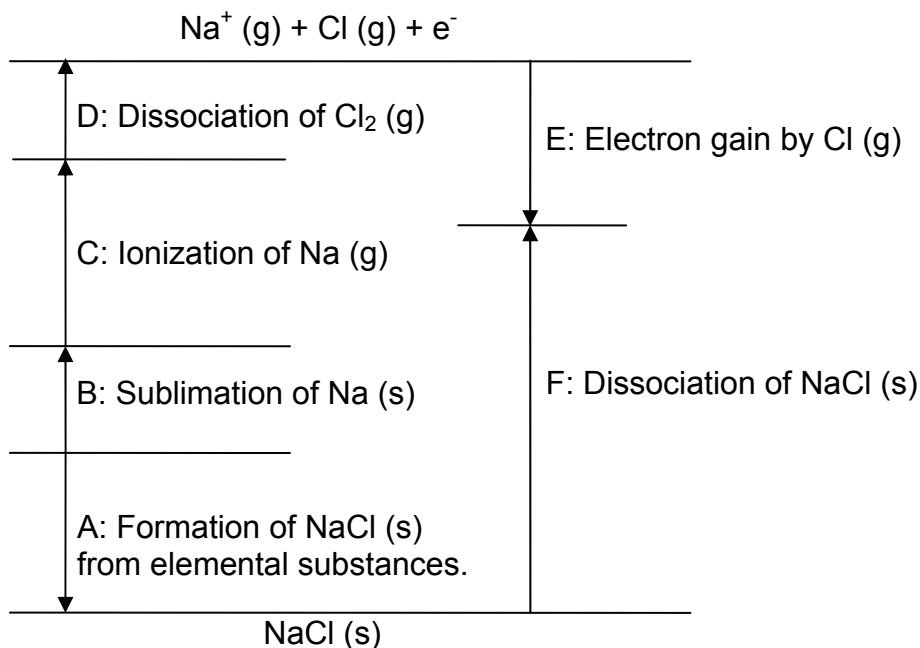
Density of NaCl crystal (kg m^{-3}): $2.14 \times 10^3 \text{ kg m}^{-3}$



Born-Haber cycle and lattice enthalpy

In ionic inorganic compounds such as sodium chloride, the heat of lattice formation from gaseous ions is very high, and the contribution of the change in entropy is small. Therefore, the lattice formation enthalpy is estimated from enthalpy data by using a Born-Haber cycle.

- c) The figure below shows the Born-Haber cycle of NaCl. The labels “g” and “s” represent “gas” and “solid” states respectively. Show chemical equations in the A and F steps.



- d) Calculate the enthalpy of the lattice formation of NaCl [kJ mol^{-1}] by using the following enthalpy data of the respective steps in the above Born-Haber cycle.

Formation of NaCl (s)	Sublimation of Na (s)	Ionization of Na (g)	Dissociation of Cl_2 (g)	Electron gain by Cl (g)
-411 kJ mol^{-1}	109 kJ mol^{-1}	496 kJ mol^{-1}	242 kJ mol^{-1}	-349 kJ mol^{-1}

[Total 3 pts]

Enthalpy conservation condition: $-\text{A} + \text{B} + \text{C} + \text{D}/2 = \text{F} - \text{E}$ [1 pt]

From the above equation, $-(-411) + 109 + 496 + (242/2) = \text{F} + 349$, thus, $\text{F} = 788$ [1 pt]

The lattice formation enthalpy of NaCl is $-\text{F}$, thus, -788 kJ mol^{-1} [1 pt]

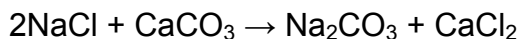
Lattice formation enthalpy of NaCl (kJ mol^{-1}): -788 kJ mol^{-1}



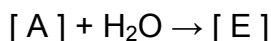
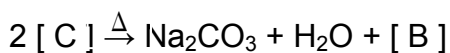
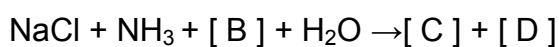
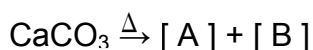
Synthesis of sodium carbonate by the ammonia-soda process (Solvay process)

Sodium carbonate (anhydrous soda ash) is a raw material in the manufacture of glass, medicaments, alkaline detergents, etc.

e) The total chemical reaction in the ammonia-soda process is represented as follows:



This reaction between sodium chloride and calcium carbonate does not proceed directly. The process comprises the following five reactions involving ammonia:



where Δ represents applying heat treatment. Insert the chemical formulas of the appropriate compounds in the blank spaces [A]–[E] in the above reactions.

A: **CaO**

B: **CO₂**

C: **NaHCO₃**

D: **NH₄Cl**

E: **Ca(OH)₂**

[Total 5 pts]

1 pt for one correct chemical formula.



Problem 3

7% of the total

3a	3b	3c	3d	Task 3
2	3	1	3	9

The chemical oxygen demand (COD) refers to the amount of oxidizable substance, such as organic compounds, in a sample solution, and it is used as an indication of water quality in seas, lakes, and marshes. For example, the COD of service water is kept below 1 mg L^{-1} . The COD (mg L^{-1}) is represented by mass of O_2 (mg) which accepts the same amount of electrons which would be accepted by the strong oxidizing agent when 1 L of a sample solution is treated with it. An example of the operation is presented below.

Analytical Operation

A 1.00-L sample solution was acidified with a sufficient amount of sulfuric acid, and chloride ions were removed by the addition of silver nitrate solution. To the sample solution, $1.00 \times 10^{-1} \text{ L}$ of $5.00 \times 10^{-3} \text{ mol L}^{-1}$ potassium permanganate solution was added, and the mixture was heated for 30 min. Further, $1.00 \times 10^{-1} \text{ L}$ of $1.25 \times 10^{-2} \text{ mol L}^{-1}$ disodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$ or NaOOC-COONa) standard solution was added, and the mixture was stirred well. Oxalate ions that remained unreacted were titrated with $5.00 \times 10^{-3} \text{ mol L}^{-1}$ potassium permanganate solution; $3.00 \times 10^{-2} \text{ L}$ of the solution was used for the titration.

- a) Give the equation of the redox reaction of potassium permanganate and disodium oxalate.



or



or



[Total 2 pts]

- b) Calculate the amount of O_2 (mg) that will oxidize the same number of moles of oxidizable substance as $1.00 \times 10^{-3} \text{ L}$ of $5.00 \times 10^{-3} \text{ mol L}^{-1}$ potassium permanganate does.

The reactions of potassium permanganate and O_2 are as follows:





Hence, 1 mol of KMnO_4 amounts to 1.25 mol of O_2 .

$$\underline{5 \times 5.00 \times 10^{-3} \text{ (mol L}^{-1}\text{)} \times 10^{-3} \text{ (L)} = 4 \times X / 32 \text{ (mol)}} \quad \text{[Underlined (or equivalent) equation: 2 pt]}$$

where X is the amount of O_2 (g).

Thus, $X = 2.00 \times 10^{-4} \text{ g.} \quad \rightarrow \quad 2.00 \times 10^{-1} \text{ mg}$

[1 pt]

[Total 3 pts]

c) From the following choices, select the most appropriate reason for the removal of chloride ions:

- [A] Some of the chloride ions react with potassium permanganate, resulting in an error in COD.
[B] Some of the chloride ions react with disodium oxalate, resulting in an error in COD.
[C] Some of the chloride ions react with organic compounds in the sample solution, resulting in an error in COD.
[D] A color is developed during titration, resulting in an error in COD.

[A]

[Total 1 pt]

d) Calculate the COD (mg L^{-1}) of the sample solution described in the analytical operation above.

The amounts of electron used for reduction and oxidation are equal, then

$$\underline{5 \times 5.00 \times 10^{-3} \text{ (mol L}^{-1}\text{)} \times (1.00 \times 10^{-1} + A) \text{ (L)} =} \quad \text{[Underlined (or equivalent) equation: 2 pt]}$$
$$\underline{2 \times 1.25 \times 10^{-2} \text{ (mol L}^{-1}\text{)} \times 1.00 \times 10^{-1} \text{ (L)} + X} \quad (1)$$

where A (mL) is the amount of potassium permanganate used for the final titration, and X (mol) is the amount of electron for the oxidizable substance.

Eq.(1) gives $X = 2.50 \times 10^{-2} \times A$.

At $A = 3.00 \times 10^{-2} \text{ (L)}$, $X = 7.50 \times 10^{-4} \text{ (mol)}$.

Hence, $\text{COD} = (32/4) \text{ (g mol}^{-1}\text{)} \times 7.50 \times 10^{-4} \text{ (mol)} \times 10^3 \text{ (mg/g)} \times 1/1 \text{ (L}^{-1}\text{)}$
 $= 6.00 \text{ mg L}^{-1}$.

[1 pt]

[Total 3 pts]

or

The amount of potassium permanganate consumed for the oxidizable substance, B (mL), is

$$\underline{5 \times 5.00 \times 10^{-3} \times (1.00 \times 10^{-1} + A - B) = 2 \times (1.25 \times 10^{-2}) \times (1.00 \times 10^{-1})} \quad [2 \text{ pt}]$$

At $A = 3.00 \times 10^{-2} \text{ L}$, B equals to $3.00 \times 10^{-2} \text{ L}$.

From the solution to question b) above,

$\text{COD} = (2.00 \times 10^{-1}) / (1.00 \times 10^{-3}) \text{ (mg/L)} \times 3.00 \times 10^{-2} \text{ (L)} \times 1/1 \text{ (L}^{-1}\text{)} = 6.00 \text{ mg L}^{-1}$ [1 pt]

[Total 3 pts]



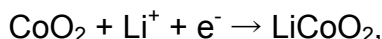
Problem 4

6% of the total

4a	4b	4c	4d	Task 4
2	3	2	1	8

The rechargeable lithium ion battery has been developed in Japan.

The standard electromotive force of the battery is 3.70 V. Assume that the half-reaction at the cathode is



and the half-reaction at the anode is



- a) Write the total reaction equation of the battery and calculate the value of the standard Gibbs energy of the reaction [kJ mol^{-1}].

Total reaction equation:



The standard Gibbs energy of the reaction:

$$\Delta G^0 = -nFE^0 = -1 \times 96485 \text{ C mol}^{-1} \times 3.70 \text{ V} = \underline{-357 \text{ kJ mol}^{-1}} \quad (1 \text{ pt})$$

- b) The battery cell is constructed using LiCoO_2 and graphite (C) as the electrode materials. Calculate the mass of the anode in the completely charged state and that in completely discharged state if 10.00 g of LiCoO_2 and 10.00 g of graphite (C) are present initially.

In the completely charged state: 10.71 g (2 pt)

The amount of LiCoO_2 is $10.00/97.87 = 0.1022 \text{ mol}$.

The amount of C is $10.00/12.01 = 0.8326 \text{ mol}$, which is larger than $0.1022 \text{ mol} \times 6 = 0.6132 \text{ mol}$.

Thus, the mass in the completely charged state of the anode is $10.00 + 0.1022 \times 6.94 = 10.709 \text{ g} = \underline{10.71 \text{ g}}$.

In the completely discharged state: 10.00 g (1 pt)



- c) Calculate the maximum energy generated per mass of the lithium ion battery cell [kJ kg^{-1}]. Assume that the correct ratio for complete reaction between the cathode and anode materials is used and the sum of the mass of electrodes is 50.0% of the total mass of the battery cell. In comparison, the energy density of lead-acid batteries used for vehicles is about 200 kJ kg^{-1} .

The mass of 1 mol LiCoO_2 is 97.87 g

The mass of 6 mol C is $12.01 \times 6 \text{ g} = 72.06 \text{ g}$

The total mass of the electrode is $(97.87 + 72.06) \text{ g} = 169.93 \text{ g}$

The mass of the cell is $169.93 / 0.500 \text{ g} = 340 \text{ g}$

The maximum energy generated is 357 kJ.

Thus, the maximum energy per unit mass of the cell is 1050 kJ kg^{-1} (2 pts)

- d) Because an aqueous solution cannot be used as an electrolyte, an organic solution is used in the lithium ion battery cell. Give the chemical formula of the gas generated if water is present in the electrolyte.

H_2 or H_2 and O_2 (1 pt)

Problem 5

7% of the total

5a-1	5a-2	5b	5c	5d	5e	5f	Task 5
1	1	2	2	3	4	5	18

When an atom X absorbs radiation with a photon energy greater than the ionization energy of the atom, the atom is ionized to generate an ion X^+ and the electron (called a photoelectron) is ejected at the same time. In this event, the energy is conserved as shown in Figure 1, that is,

Photon energy ($h\nu$) = ionization energy (IE) of X + kinetic energy of photoelectron.

When a molecule, for example, H_2 , absorbs short-wavelength light, the photoelectron is ejected and an H_2^+ ion with a variety of vibrational states is produced. A photoelectron spectrum is a plot of the number of photoelectrons as a function of the kinetic energy of the photoelectrons. Figure 2 shows a typical photoelectron spectrum when H_2 in the lowest vibrational level is irradiated by monochromatic light of 21.2 eV. No photoelectrons are detected above 6.0 eV. eV is a unit of energy and 1.0 eV is equal to 1.6×10^{-19} J.

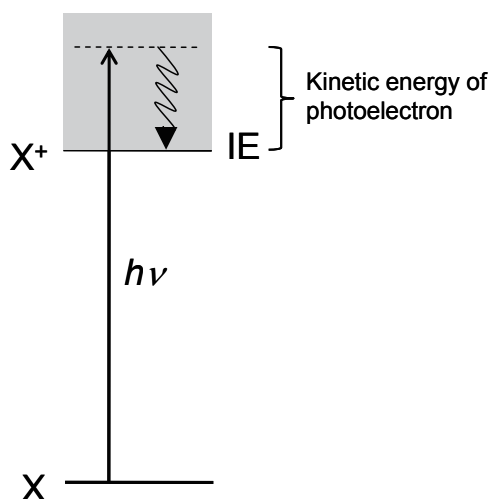


Figure 1. Schematic diagram of photoelectron spectroscopy.

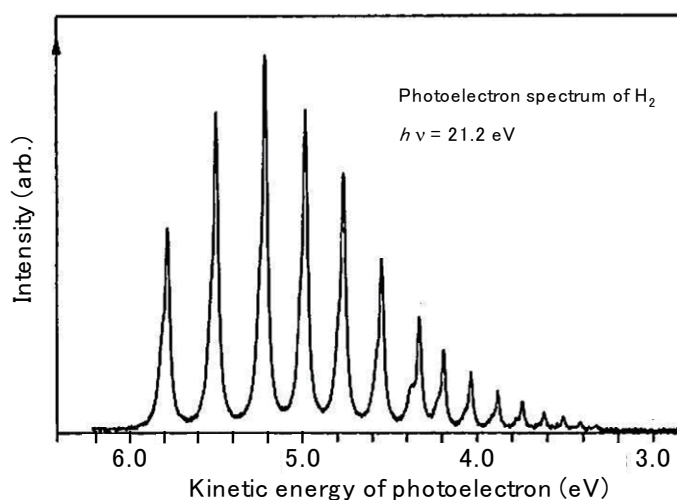


Figure 2. Photoelectron spectrum of H_2 . The energy of the incident light is 21.2 eV.



a-1) Determine the energy difference ΔE_{A1} (eV) between H_2 ($v = 0$) and H_2^+ ($v_{ion} = 0$) to the first decimal place. v and v_{ion} denote the vibrational quantum numbers of H_2 and H_2^+ , respectively.

a-2) Determine the energy difference ΔE_{A2} (eV) between H_2^+ ($v_{ion} = 0$) and H_2^+ ($v_{ion} = 3$) to the first decimal place.

a-1) & a-2)

The spectral peak at 5.8 eV in Fig. 2 corresponds to the electron with the highest kinetic energy, which is generated by the reaction $H_2(v = 0) \rightarrow H_2^+(v_{ion} = 0) + e$. Accordingly,

$$\Delta E_{A1} = 21.2 \text{ eV} - 5.8 \text{ eV} = 15.4 \text{ eV}$$

One can estimate from Fig. 2 that the energy difference ΔE_{A2} between H_2^+ ($v_{ion} = 0$) and H_2^+ ($v_{ion} = 3$) is approximately 0.8 eV.

$$\Delta E_{A1} \text{ (eV)} = 15.4 \text{ eV} \quad 1 \text{ pt}$$

$$\Delta E_{A2} \text{ (eV)} = 0.8 \text{ eV} \quad 1 \text{ pt}$$

b) The electronic energy levels E_n^H of a hydrogen atom are given by the equation

$$E_n^H = -\frac{Ry}{n^2} \quad (n = 1, 2, 3, \dots)$$

Here n is a principal quantum number, and Ry is a constant with dimensions of energy. The energy from $n = 1$ to $n = 2$ of the hydrogen atom is 10.2 eV. Calculate the ionization energy E_B (eV) of the hydrogen atom to the first decimal place.

The ionization energy corresponds to $n = \infty$. Accordingly,

$$\Delta E_{n=2 \leftarrow n=1} = \frac{3}{4} Ry$$

$$\Delta E_{n=\infty \leftarrow n=1} = Ry$$

Thus, the energy required for the ionization is 4/3 times larger than the transition energy of the Lyman α line.

$$E_B = 10.2 \text{ eV} \times \frac{4}{3} = 13.6 \text{ eV}$$

$$E_B \text{ (eV)} = 13.6 \text{ eV} \quad 2 \text{ pts}$$



- c) The energy threshold for the generation of two electronically excited hydrogen atoms H^* ($n = 2$) from H_2 ($v = 0$) has been derived to be 24.9 eV by an experiment. Determine the bond energy E_C (eV) of H_2 to the first decimal place.

24.9 eV = the binding energy of a hydrogen molecule + 10.2 eV + 10.2 eV.
Thus, the binding energy of a hydrogen molecule = $E_C = 4.5$ eV.

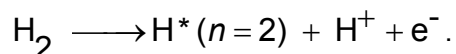
$$E_C \text{ (eV)} = 4.5 \text{ eV} \quad 2 \text{ pts}$$

- d) Considering an energy cycle, determine the bond energy E_D (eV) of H_2^+ to the first decimal place. If you don't have the values for E_B and E_C , then use 15.0 eV and 5.0 eV for E_B and E_C , respectively.

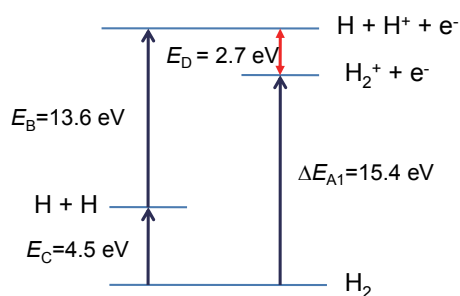
From Figure 3 below,
 $E_D = E_B + E_C - \Delta E_{A1} = 13.6 + 4.5 - 15.4 = 2.7$ eV.

$$E_D \text{ (eV)} = 2.7 \text{ eV} \quad 3 \text{ pts}$$

- e) Calculate the threshold energy E_E (eV) of the following dissociative ionization reaction to the first decimal place:



If you don't have the values for E_B and E_C , then use 15.0 eV and 5.0 eV for E_B and E_C , respectively.

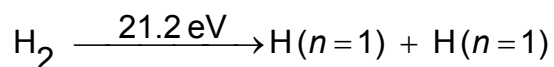


From Figure 3 above, the threshold energy for the dissociative ionization reaction $H_2 \rightarrow H^* (n = 2) + H^+ + e^-$ is $E_B + E_C + 10.2$ eV = $13.6 + 4.5 + 10.2 = 28.3$ eV.

$$E_E \text{ (eV)} = 28.3 \text{ eV} \quad 4 \text{ pts}$$



- f) When H_2 absorbs monochromatic light of 21.2 eV, the following dissociation process occurs at the same time.



Two hydrogen atoms move in opposite directions with the same speed. Calculate the speed u (m s^{-1}) of the hydrogen atoms generated in the above reaction. H_2 is assumed to be at rest. If you don't have the value for E_C , then use 5.0 eV for E_C .

The excess energy is 16.7 eV ($= 21.2 \text{ eV} - 4.5 \text{ eV}$). Because two hydrogen atoms are generated upon photodissociation, half of this excess energy is released as translational energy of the hydrogen atoms.

$$\frac{1}{2}mu^2 = 8.35 \text{ eV} = 1.34 \times 10^{-18} \text{ J}$$

(2 pts)

$$m = \frac{1.008 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.67 \times 10^{-27} \text{ kg}$$

Then,

$$u^2 = 1.6 \times 10^9 \text{ m}^2 \text{ s}^{-2} \quad u \approx 4.0 \times 10^4 \text{ m s}^{-1}$$

$$u \text{ (m/s)} = 4.0 \times 10^4 \text{ m/s} \quad 5 \text{ pts}$$

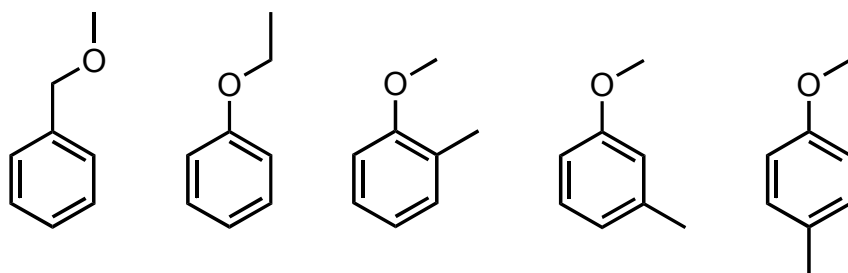
Problem 6

6 % of the total

6a	6b	6c	6d	Task 6
5	4	6	11	26

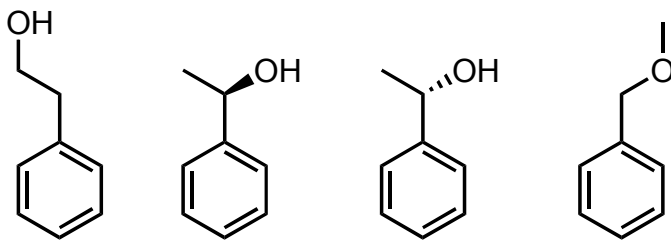
Read the description of four kinds of isomeric organic compounds of **A**, **B**, **C**, and **D**. All have $C_8H_{10}O$ and contain a benzene ring. Answer the questions that follow. If there are stereoisomers, give all structural formulas. Note that any wrong isomers will be penalized.

- (1) At room temperature, a piece of sodium metal was added to **A**, **B**, and **C** in test tubes and the evolution of hydrogen gas was observed only in the case of **C**.
 - When an iron(III) chloride aqueous solution was added to **C** and **D**, no coloration was observed in **C**, whereas **D** was colored.
 - **A** was oxidized when (2) aqueous potassium permanganate was added to it and the mixture was heated; the acidification of the heated mixture and its isolation afforded benzoic acid.
 - Let's imagine that (3) a hydrogen atom in the benzene ring is replaced by a chlorine atom, it is possible to obtain four kinds of monochlorinated structural isomers from **B**, while only two kinds of such isomers can be obtained from **D**.
 - Hydrogenation of the benzene ring in **C** and **D** using a catalyst gave saturated alcohol(s). It was found that the saturated alcohol(s) obtained from **C** has no stereogenic carbons, but the one(s) from **D** has stereogenic carbon(s).
- a) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that do NOT yield hydrogen gas in the underlined procedure (1), in which a piece of sodium is added to the neat samples in the case of the liquid samples and to the concentrated solution of the samples in an aprotic solvent in the case of the solid ones.



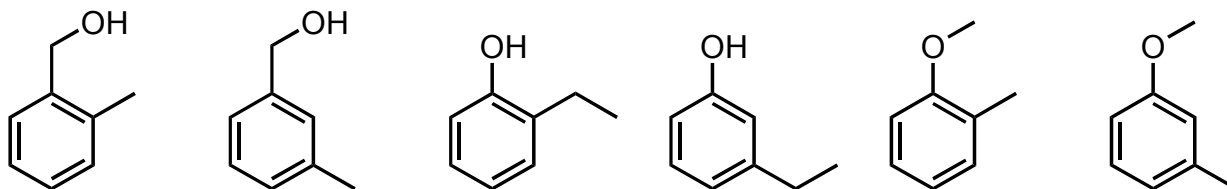
1pt each
wrong isomer: -1pt each
total pts ≥ 0 (not negative)

- b) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that yield benzoic acid in the underlined procedure (2).



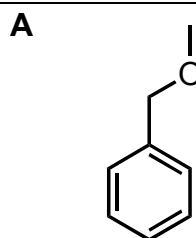
1pt each
wrong isomer: -1pt each
total pts ≥ 0 (not negative)

- c) Among all the isomeric organic compounds of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that could yield four different mono-chlorinated structural isomers when the underlined transformation in (3) is performed.

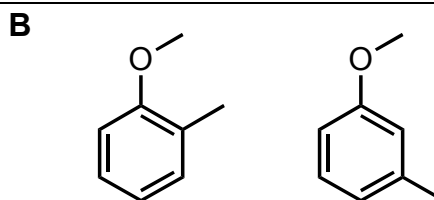


1pt each
wrong isomer: -1pt each
total pts ≥ 0 (not negative)

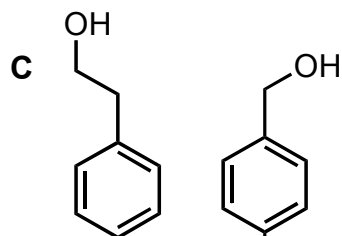
- d) Give the structural formulas of **A**, **B**, **C**, and **D**. When several isomers can be considered, give the structural formulas of all of them.



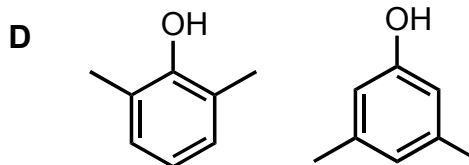
1pt
wrong isomer: -1pt each
total pts ≥ 0 (not negative)



1pt each
wrong isomer: -1pt each
total pts ≥ 0 (not negative)



2pts each
wrong alcohol/phenol: -1pt each
ether: -2pts each
total pts ≥ 0 (not negative)



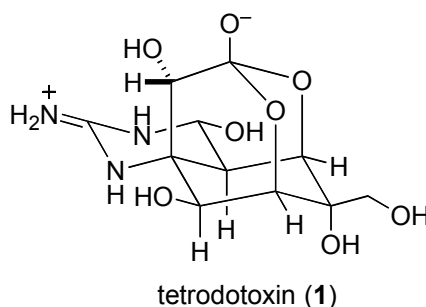
2pts each
wrong alcohol/phenol: -1pt each
ether: -2pts each
total pts ≥ 0 (not negative)

Problem 7

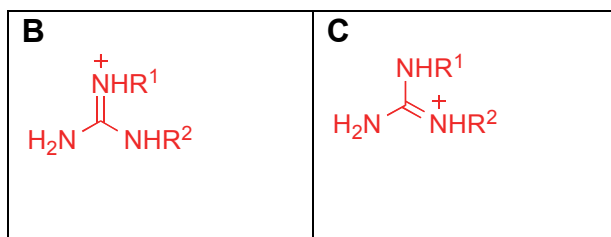
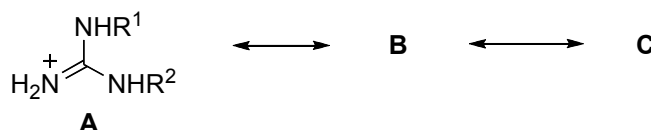
7% of the total

7a	7b	7c	7d	Task 7
4	9	6	5	24

Certain varieties of puffer fish, *Fugu* in Japanese, are highly prized as foods in Japan. Since the viscera (especially ovaries and livers) of the fish contain a potent toxin (tetrodotoxin), food poisoning often results from its ingestion. Studies on tetrodotoxin (**1**) have been performed from the beginning in the 20th century; its chemical structure was elucidated in 1964.

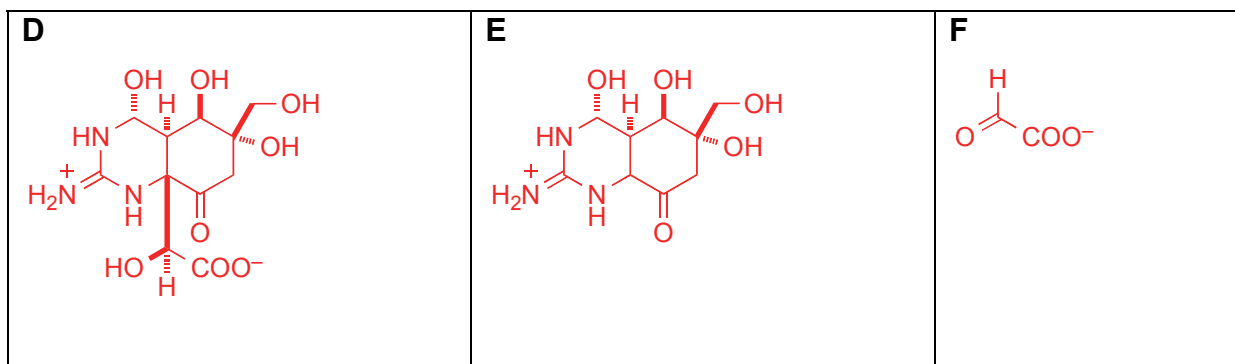
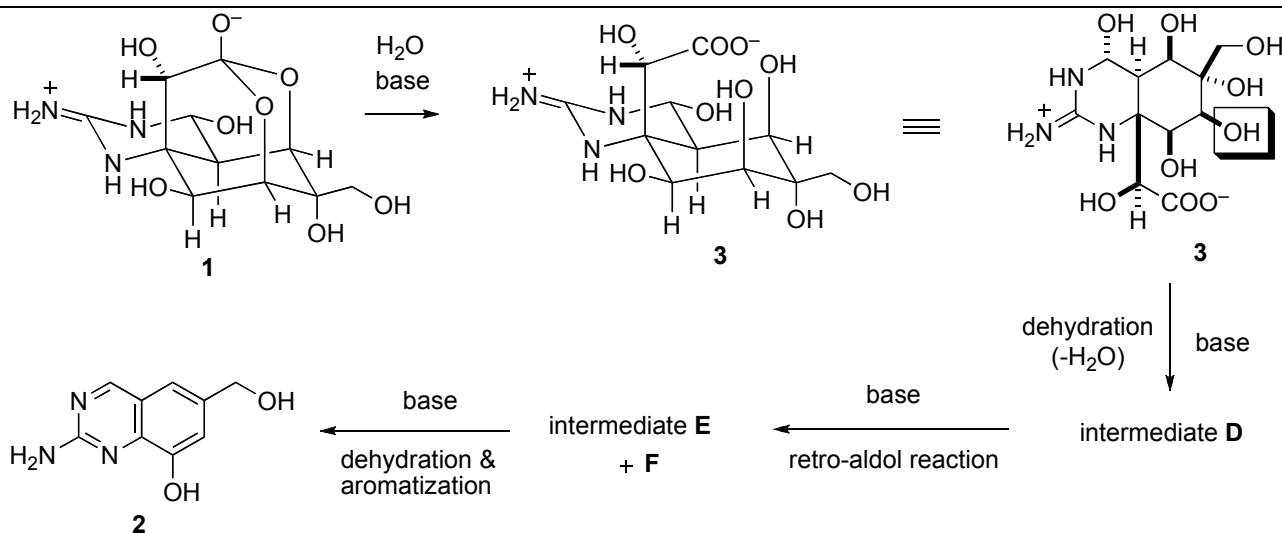


- a) The guanidine group in tetrodotoxin exhibits strong basicity. The guanidinium ion resulting from protonation on the guanidine group is stabilized by the existence of the following resonance. Draw two resonance structures **B** and **C**.



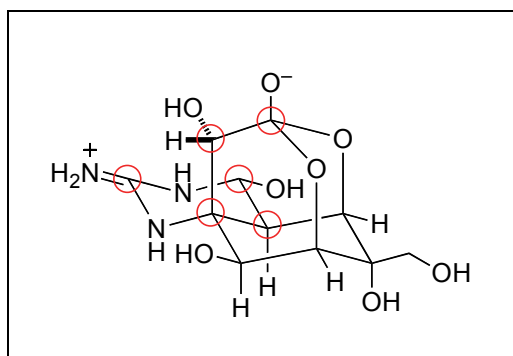
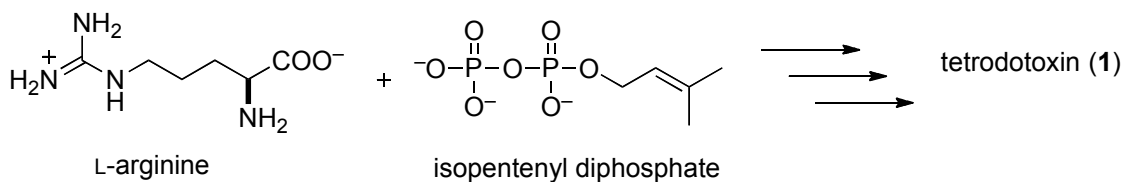
2 pts each.

- b) Many derivatization reactions were performed in structure studies of tetrodotoxin. Treatment of tetrodotoxin (**1**) with ethanolic potassium hydroxide upon heating afforded quinazoline derivative **2**, which provided an insight into the nature of the fundamental skeleton of tetrodotoxin. The reaction mechanism can be described as follows. First, tetrodotoxin is hydrolyzed into carboxylate **3**. Then the hydroxyl group highlighted with a frame is eliminated by the base to give intermediate **D**. A retro-aldol reaction of **D** cleaves a carbon-carbon bond to provide intermediates **E** and **F**. Finally, dehydration and aromatization from **E** produce quinazoline derivative **2**. Draw structures of the postulated intermediates **D**, **E**, and **F**.



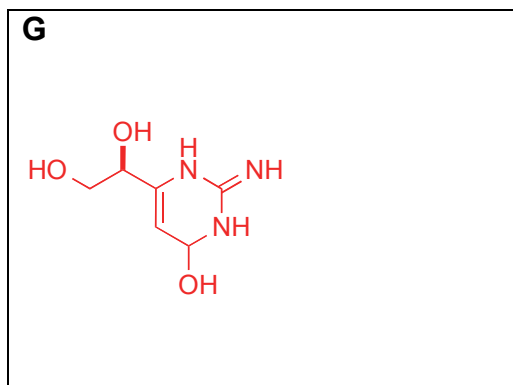
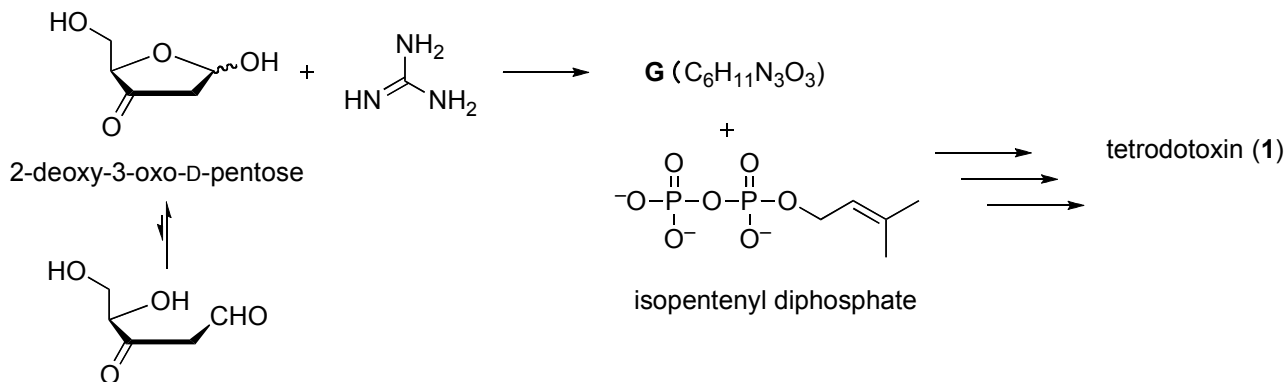
3 pts each. Other stereoisomers are acceptable. Each free form is acceptable. Tautomers concerning guanidinium moiety are all acceptable. Enol form is acceptable. E: dehydrated products and zwitterionic structure are acceptable.

- c) Although biosynthesis of tetrodotoxin still remains to be clarified, it is proposed that tetrodotoxin may be biologically synthesized from L-arginine and isopentenyl diphosphate. Among the carbons included in tetrodotoxin, circle all the carbons that are expected to be of L-arginine origin.

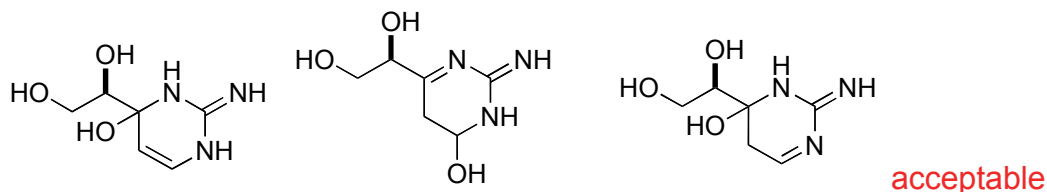


6 pts. 1 pt each for correct carbon. Deduct 1 pt for each carbon over 6. 0 pts for all carbons circled.

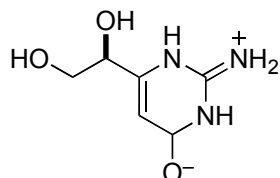
- d) In the 1990s, an alternative biosynthetic pathway of tetrodotoxin was proposed. Condensation between 2-deoxy-3-oxo-D-pentose and guanidine provides intermediate **G** with cyclic guanidine moiety (molecular formula $C_6H_{11}N_3O_3$). Tetrodotoxin may be biologically synthesized from intermediate **G** and isopentenyl diphosphate. Draw a structure of the postulated intermediate **G** showing the stereochemistry.



5 pts (enantiomer at C4, 3 pts, C4 stereochemistry is unclear, 3 pts).



Each zwitterionic structure (and protonated structure) like below is acceptable.



Tautomers concerning guanidine moiety are all acceptable.



Problem 8

6% of the total

8a-1	8a-2	8a-3	8b-1	8b-2	Task 8
2	4	3	4	7	20

The esterification reaction between bi-functional molecules gives one of the typical linear chain polymers as shown in eq.(1) by polycondensation (often called “condensation polymerization”). The control of polymerization conditions and procedures determines the length of polymer strands, i.e., *the average degree of polymerization*, X (note that $X = 2n$ in the present instance). Because X (and also n) is an averaged number, it is not always an integer but a value with decimal figures.



X can be estimated from the consumption of functional groups (here, -COOH and -OH). Let us define the degree of reaction, p , as $p = (N_0 - N) / N_0 (\leq 1)$, where N_0 and N denote the total numbers of functional groups before and after the polymerization, respectively. For each functional group of the dicarboxylic acid molecules (**A**) and diol molecules (**B**), we add the suffixes of “A” or “B” such as N_{A0} , N_{B0} , N_A or N_B , respectively, i.e., $N_0 = N_{A0} + N_{B0}$ and $N = N_A + N_B$. When the initial feed is unbalanced such as $N_{A0} \leq N_{B0}$, X is expressed by p_A and r as shown in eq.(2), where $r = N_{A0} / N_{B0} (\leq 1)$ and $p_A = (N_{A0} - N_A) / N_{A0}$. If $r = 1$, p_A is identical to p and eq.(2) becomes the same to the Carothers equation.

$$X = (1 + r) / (1 + r - 2p_A r) \quad (2)$$

a) Some nylon-6,6 sample was prepared by polycondensation between an *equimolar* mixture of adipic acid (hexanedioic acid) and hexamethylenediamine (hexane-1,6-diamine).

a-1) Show the chemical structure of this nylon-6,6 sample. [Caution: what are the end groups when polycondensation was started from the *equimolar* mixture?]

HO-[CO(CH₂)₄CO-NH(CH₂)₆NH]_n-H or equivalent structures are all OK.
Total 2 pts. -0.5 pt for lacking “n,” another -0.5 pt for lacking each of the end group(s).



- a-2) When this nylon-6,6 sample carries an average molecular weight, M , of 5507.25 (g mol^{-1}), give its X value to the second decimal place.

Calculation procedures must be shown by suitable equation(s) (otherwise, no score will be provided):

The unit molecular weight, M_u , is calculated to be,

$$M_u = (12.01 \times 12 + 1.01 \times 22 + 14.01 \times 2 + 16.00 \times 2) / 2 = 226.36 / 2 = 113.18$$

$$X = (5507.25 - 18.02) / M_u = (5507.25 - 18.02) / 113.18 = 48.50, \text{ or}$$

$$X = 2n = 2 \times [(5507.25 - 18.02) / 226.36] = 48.50$$

$$X = 48.50$$

Black parts are prewritten in the answer boxes (same to all questions in Problem 8). Underlined (or equivalent) calculation procedures are required. Total 4 pts. -1 pt for calculation mistakes.

- a-3) Give the p value necessary to prepare this nylon-6,6 sample of $M = 5507.25$ (g mol^{-1}) to the fifth decimal place. If you get no numerical answer in a-2), use 52.50 instead.

From eq.(3) at $r = 1$ (Carothers eq.), $X = 48.50 = 1 / (1 - p)$, then $p = 0.97938_1$
 $\doteq 0.97938$

$$p = 0.97938 \text{ (0.98095 when } X = 52.50.)$$

Total 3 pts. -1 pt for calculation mistakes.

- b) The low-molecular-weight polyester (oligoester) is prepared from the mixture of 36.54 (g) of adipic acid (hexanedioic acid) and an unknown amount [W (g)] of butane-1,4-diol (Bdiol). Under the condition of $p_A \rightarrow 1$, the oligoester with $X = 11.00$ carrying Bdiol units in both chain ends is obtained.

- b-1) Show the *precise* chemical structure of this oligoester of $X = 11.00$.

$[\text{HO}(\text{CH}_2)_4\text{O}]_{1.000}-[\text{CO}(\text{CH}_2)_4\text{CO}-\text{O}(\text{CH}_2)_4\text{O}]_{5.000}-\text{H}$ or
 $\text{HO}(\text{CH}_2)_4\text{O}-[\text{CO}(\text{CH}_2)_4\text{CO}-\text{O}(\text{CH}_2)_4\text{O}]_{5.000}-\text{H}$ is accurate, however,
 $\text{HO}(\text{CH}_2)_4\text{O}-[\text{CO}(\text{CH}_2)_4\text{CO}-\text{O}(\text{CH}_2)_4\text{O}]_5-\text{H}$ is acceptable.

Total 4 pts, -1 pt for lacking the number of unit repeating or writing " n " instead of "5.00 (or 5)". Another -1 pt for lacking HO- and/or -H end group(s). No point if lacking the left-most $\text{HO}(\text{CH}_2)_4\text{O}-$ group.



b-2) Calculate the unknown amount, W (g), to the first decimal place.

Calculation procedures must be shown by suitable equation(s) (otherwise, no score will be provided):

$$M_w(\text{adipic acid}) = 146.16, M_w(\text{Bdiol}) = 90.14$$

Ans.1 Since $X = 11.00$, the oligoester contains 5.00 units of adipate and 6.00 units of Bdiol. [cf) $5.00 + 6.00 = 11.00 = X$] When $p_A \rightarrow 1$, the initial molar feed ratio of the monomers is equal to the molar composition of the resulting oligoester.

$$[\text{adipic acid}]_0 / [\text{Bdiol}]_0 = 5.00 / 6.00, \underline{W = 90.14 \times (6.00 / 5.00) \times (36.54 / 146.16) = 27.042 \doteq 27.0 \text{ (g)}}$$

Ans.2 From eq.(2), when $p_A \rightarrow 1$, $X = (1 + r) / (1 - r)$. Therefore,

$$\underline{11.00 = [1 + \{(36.54 / 146.16) / (W / 90.14)\}] / [1 - \{(36.54 / 146.16) / (W / 90.14)\}]} \\ = [(W / 90.14) + 0.2500] / [(W / 90.14) - 0.2500]$$

$$\underline{11.00 \times [(W / 90.14) - 0.2500] = [(W / 90.14) + 0.2500]}, \underline{10.00 \times (W / 90.14) = 3.000}$$

$$\underline{W = 3.000 \times 90.14 / 10.00 = 27.042 \doteq 27.0 \text{ (g)}}$$

$$\underline{W = 27.0 \text{ (g)}}$$

Either calculation procedures are acceptable. Underlined (or equivalent) calculation procedures are required. Total 7 pts, -1 pt for calculation mistakes.

Problem 9

7% of the total

9a	9b	9c	9d	9e	9f	Task 9
4	2	8	4	8	8	34

α -Cyclodextrin (α CyD), which is a cyclic oligosaccharide of six $\alpha(1 \rightarrow 4)$ linked α -D-glucopyranoside units, can be topologically represented as toroids (Figure 1). α -D-glucopyranoside units in α CyD are usually in the most stable chair conformation.

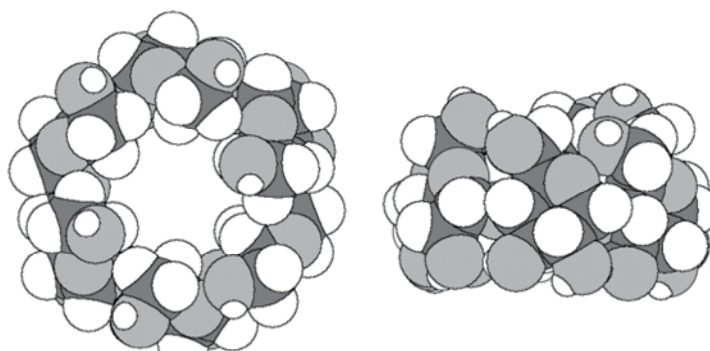
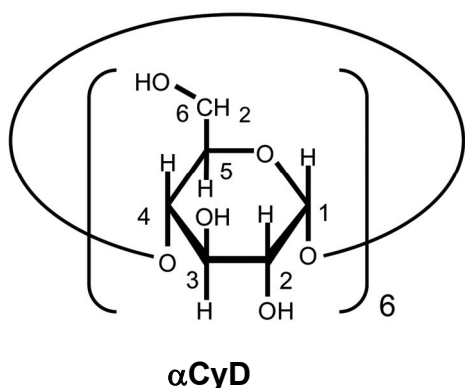
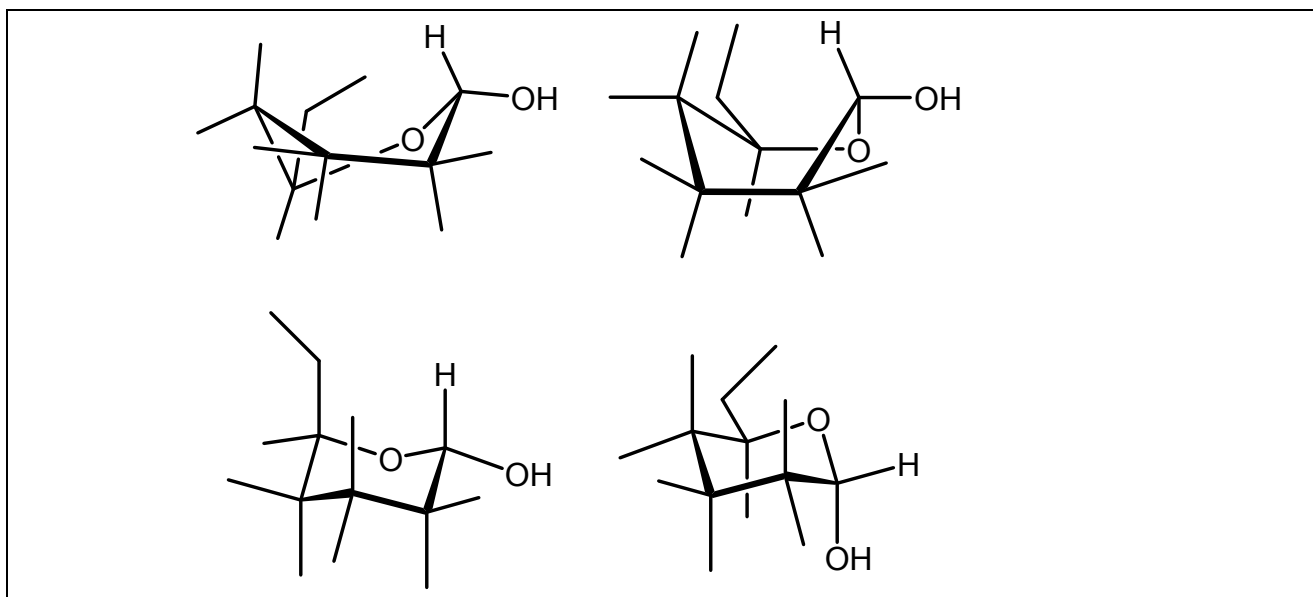


Figure 1. Space filling model of α CyD. Left: view through the hole. Right: side view.

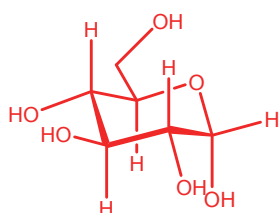
- a) Give the absolute configuration (*R* or *S*) at stereogenic carbons C-2 and C-5 of D-glucose. Also, draw a stereostructure of the open chain form of D-glucose.

Absolute configuration at C-2: <div style="display: flex; justify-content: space-between; align-items: center;"> <i>R</i> 1 pt </div>	Chain form: <div style="text-align: center; margin-top: 10px;"> 2 pts (carbon skeleton: 1 pt; others: 1 pt) </div>
Absolute configuration at C-5: <div style="display: flex; justify-content: space-between; align-items: center;"> <i>R</i> 1 pt </div>	

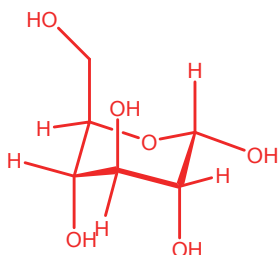
- b) Choose the most stable conformation from the four incomplete α -D-glucopyranose formulas given in the answer box and enclose it in a box. Also, add four OH groups and four H atoms to complete the α -D-glucopyranose formula.



Answer:



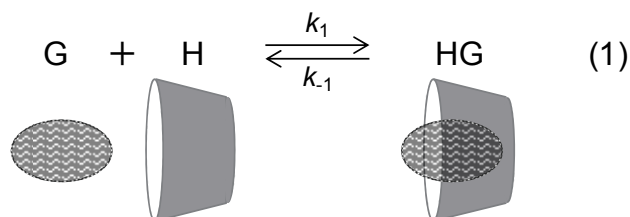
2 pts (4C_1 : 1 pt; -OH: 1 pt)



1 pts (4C_1 : 0 pt; -OH: 1 pt)

Others 0 pt

α CyD in water is able to host hydrophobic molecules. When the host/guest (H/G) stoichiometry is 1/1, the inclusion complexation can be given by the following equilibrium.



where k_1 and k_{-1} are the rate constant for the forward and backward reaction, respectively. The complexation of a guest to α CyD causes a chemical shift change in ^1H NMR spectra. Figure 2 shows a part of ^1H NMR spectra (signals from H-1 of α CyD) showing the chemical shift change in the presence of varying amounts of 1,10-bis(trimethylammonium)decane diiodide (BTAD). The doublet peak at 5.06 ppm is from H-1 of free α CyD, while the doublet at 5.14 ppm is from H-1 of α CyD complexed with BTAD. (Note that the spectra given in Figure 2 were measured in the complexation equilibrium state.)

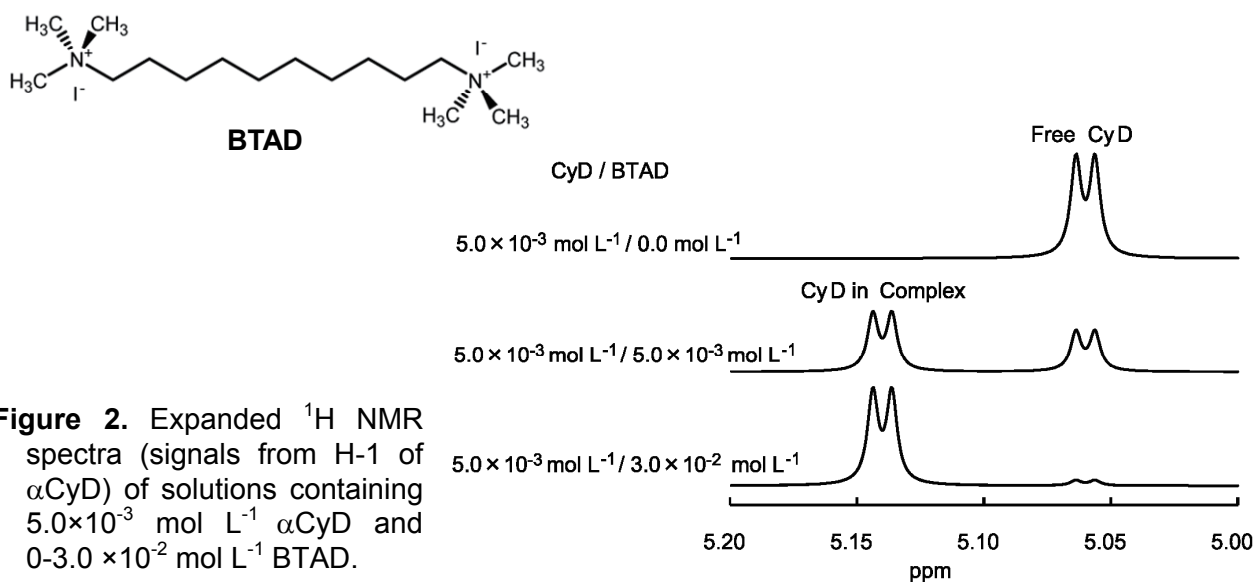


Figure 2. Expanded ^1H NMR spectra (signals from H-1 of α CyD) of solutions containing $5.0 \times 10^{-3} \text{ mol L}^{-1}$ α CyD and $0-3.0 \times 10^{-2} \text{ mol L}^{-1}$ BTAD.

- c) In the spectrum of $5.0 \times 10^{-3} \text{ mol L}^{-1} / 5.0 \times 10^{-3} \text{ mol L}^{-1}$ α CyD/BTAD, the relative peak areas of the doublets at 5.06 and 5.14 ppm are 0.41 and 0.59, respectively. Calculate, to 2 significant figures, the concentration equilibrium constant, K for the inclusion complexation of α CyD/BTAD.

$$K = \frac{[\text{HG}]}{[\text{H}][\text{G}]} = \frac{[\alpha\text{CyD}]_0 \times a_{5.14}}{[\alpha\text{CyD}]_0 \times a_{5.06} \times \{[\text{BTAD}]_0 - [\alpha\text{CyD}]_0 \times a_{5.14}\}} = \frac{5.0 \times 10^{-3} \text{ M} \times 0.59}{(5.0 \times 10^{-3} \text{ M} \times 0.41)^2} = 0.70 \times 10^3$$

1 pt

3 pts

3 pts

1 pt

$a_{5.06}$: relative area of the peak at 5.06 ppm = mole fraction of free α CyD

$a_{5.14}$: relative area of the peak at 5.14 ppm = mole fraction of α CyD complexed with BTAD

K: 7.0×10^2

8 pts in total

Complexation of α CyD with hexyltrimethylammonium bromide (HTAB) appears in NMR spectra in a way different from the α CyD/BTAD complexation. Figure 3 shows a part of ^1H NMR spectra (H-6 signal of HTAB) in α CyD/HTAB solutions. The signal appears as one triplet (not two triplets), which shifts depending on the concentration of α CyD from the position of free HTAB to the position of α CyD/HTAB in proportion to the fraction of the complex in the solution. The H-6 signals from free HTAB and HTAB complexed with α CyD are triplets at 0.740 ppm and 0.860 ppm, respectively.

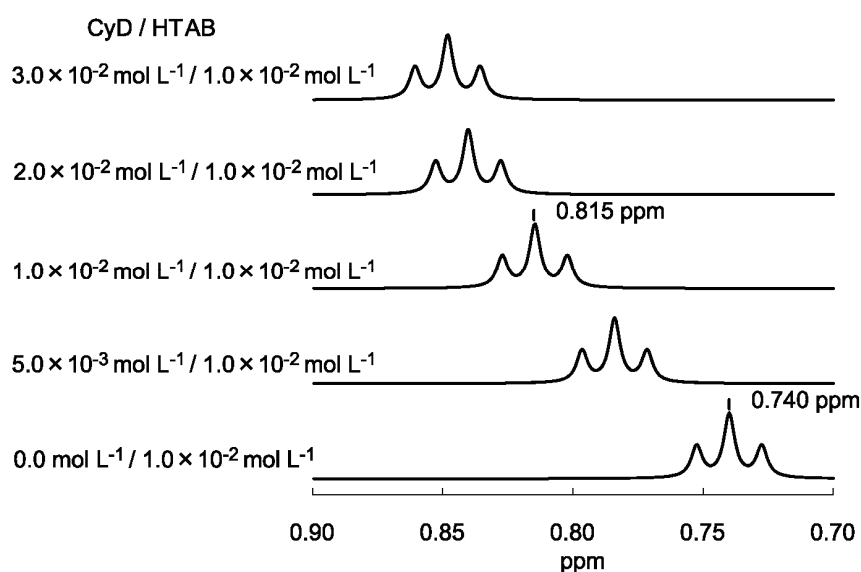
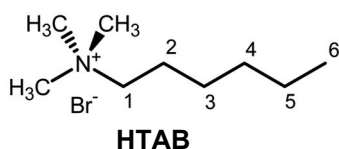


Figure 3. Expanded ^1H NMR spectra (H-6 signal of HTAB) of solutions containing $1.0 \times 10^{-2} \text{ mol L}^{-1}$ HTAB and 0 – $3.0 \times 10^{-2} \text{ mol L}^{-1}$ α CyD.

- d) The signal of HTAB in α CyD/HTAB solutions appears as one triplet, which shifts depending on the concentration of α CyD. Choose the rational interpretation(s) just from these spectra.

hint: When a guest molecule move in and out of α CyD rapidly and repeatedly, only one signal of the guest is observed at the weighted average of the chemical shifts of the free guest and the shift of the guest included in α CyD.

- k_1 of α CyD/HTAB $>$ k_1 of α CyD/BTAD
- k_1 of α CyD/HTAB $<$ k_1 of α CyD/BTAD
- K of α CyD/HTAB $>$ K of α CyD/BTAD
- K of α CyD/HTAB $<$ K of α CyD/BTAD

a 4 pts (additional choice : –2 pts for each)

