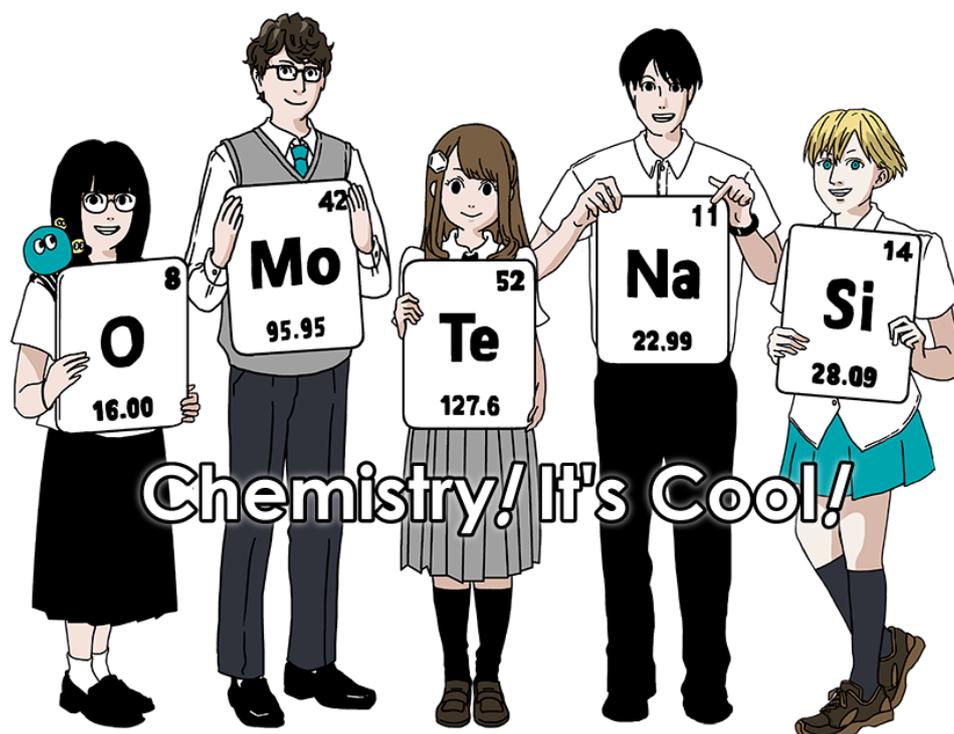




International Chemistry Olympiad 2021  
Osaka, Japan  
53<sup>rd</sup> IChO2021 Japan  
24<sup>th</sup> July – 2<sup>nd</sup> August  
<https://www.icho2021.org>



# Preparatory Problems Solutions and Comments

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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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Problem 1. Revision of SI unit

1-1.

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 = 8 \quad \underline{n = 8}$$

1-2.  $nm = a^3 d$  is modified to give:

$$\underline{d = \frac{nm}{a^3} \text{ kg m}^{-3}}$$

1-3. Combining the relationships  $nm u = a^3 d$  and  $u = 1/N_A$  yields:

$$w = \frac{4}{3} \pi r^3 d = \frac{4\pi r^3}{3} \frac{nm}{a^3} = \frac{4\pi r^3}{3} \frac{n}{a^3} 28.09 u = \frac{4\pi r^3}{3} \frac{n}{a^3} \frac{28.09 \times 10^{-3}}{N_A} \quad N_A = \underline{6.07 \times 10^{23}}$$

2-1. As the Avogadro and Planck constants are dependent on each other, having the Planck constant is the same as having the Avogadro constant.

- $N_A$  alone is sufficient     
  both  $N_A$  and  $h$  are required     
   $h$  alone is sufficient

2-2. As the Planck constant is:

$$h = 6.62607015 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1} = 6.62607015 \times 10^{-34} \times 1 \text{ kg (1 m)}^2 (1 \text{ s})^{-1},$$

we obtain:

$$1 \text{ kg} = \frac{h}{6.62607015 \times 10^{-34}} \frac{1 \text{ s}}{(1 \text{ m})^2} = \underline{1.4755214 \times 10^{40} \frac{h \Delta \nu c^2}{c^2}}$$

2-3. Given that the wavelength is correlated to the frequency according to  $c = \nu \lambda$ , mass can be calculated by:

$$m = \frac{h}{c \lambda} = \underline{3.48 \times 10^{-36} \text{ kg}}$$

Problem 2. Does water boil or evaporate?

1. When 1 mol of liquid water evaporates to water vapor at  $p_0$  [bar] the entropy change is  $\Delta S_v^\circ$ . The entropy of the water vapor at  $p_1$  [bar] is by  $-R \ln(p_1/p_0)$  larger than that at  $p_0$ . Therefore, when 1 mol of liquid water evaporates to water vapor at  $p_1$ , the change in entropy can be derived from (1) as:

$$\Delta S_v = \Delta S_v^\circ - R \ln(p_1/p_0) \quad (1')$$

2. The boiling point corresponds to the temperature where the Gibbs energy change is 0 when liquid water evaporates to water vapor at 1 bar.

From:

$$\Delta G_v = \Delta H_v^\circ - T_v \Delta S_v^\circ = 0$$

follows that:

$$T_v = \frac{\Delta H_v^\circ}{\Delta S_v^\circ} = 373.05 \text{ K} = 99.9^\circ\text{C} (100^\circ\text{C}).$$

3. The saturated vapor pressure at a given temperature is the pressure where the Gibbs energy change is 0 when water evaporates at that temperature. The Gibbs energy change when water is evaporated at a pressure  $p_1$  and temperature  $T_1$  can be derived from (1') as

$$\Delta G_v = \Delta H_v - T_1 \Delta S_v = \Delta H_v^\circ - T_1 (\Delta S_v^\circ - R \ln(p_1/p_0))$$

When  $p_1$  is equal to the saturated vapor pressure:

$$\Delta H_v^\circ - T_1 (\Delta S_v^\circ - R \ln(p_1/p_0)) = 0$$

then:

$$\Delta H_v^\circ - T_1 \Delta S_v^\circ = -RT_1 \ln(p_1/p_0) \quad (2')$$

From  $p_0 = 1$  bar,  $T_1 = 360.15$  K,  $\Delta H_v^\circ = 4.070 \times 10^4$  J mol<sup>-1</sup>, and  $\Delta S_v^\circ = 1.091 \times 10^2$  J K<sup>-1</sup> mol<sup>-1</sup>, it follows that:

$$p_1 = 0.62 \text{ bar}$$

4. The Gibbs energy change when 1 mol of liquid water evaporates at 0.5  $p_1$  of water vapor can be derived from (1') as:

$$\begin{aligned} \Delta G_v &= \Delta H_v - T_1 \Delta S_v = \Delta H_v^\circ - T_1 (\Delta S_v^\circ - R \ln(0.5 p_1/p_0)) \\ &= \Delta H_v^\circ - T_1 \Delta S_v^\circ + RT_1 \ln(p_1) - RT_1 \ln 2 = -RT_1 \ln 2 \quad [\text{from } (2')] \end{aligned}$$

For  $p_0 = 1$  bar,  $T_1 = 360.15$  K, it follows that:

$$\Delta G_v = -2.07 \text{ kJ mol}^{-1}$$

5. Before moving the piston, the partial pressure of water vapor is  $p_s(87^\circ\text{C}) = 0.62$  bar (c), the partial pressure of Ar is  $1 - 0.62 = 0.38$  bar (b), and the volume of gas is:

$$\frac{0.10 \times 8.31 \times 10^3 \times 360.15}{0.38 \times 10^5 \text{ Pa}} = 7.88 (7.9) \text{ L (d).}$$

Let  $n$  be the number of moles of water vapor:

$$62000 \text{ Pa} \times 7.88 \text{ L} = n \times 8.31 \times 10^3 \times 360.15 \text{ K}$$

$$n = 0.16 \text{ mol}$$

Therefore, the number of moles of liquid water is:

$$n_1 = 1.00 - 0.16 = 0.84 \text{ mol (e)}$$

When the piston is pulled back quickly and the volume is increased to 15.8 L, the partial pressures of water and Ar decrease to:

$$(\text{partial pressure of Ar}) = 0.38 \times \frac{7.88}{15.8} = 0.19 \text{ bar (f)}$$

$$(\text{partial pressure of water vapor}) = 0.62 \times \frac{7.88}{15.8} = 0.31 \text{ bar (g)}.$$

Here, as a realistic non-equilibrium state, it is assumed that the speed with which the piston is pulled back is sufficiently fast with respect to the speed with which water vaporizes.

Since the total pressure (0.5 bar) is smaller than the saturated vapor pressure of water  $p_s(87^\circ\text{C}) = 0.62 \text{ bar}$ , the water begins to boil. The boiling stops when the total pressure (partial pressure of Ar + partial pressure of water vapor) becomes equal to the saturated vapor pressure of water at  $87^\circ\text{C}$ :

$$0.62 \text{ bar} = 0.19 \text{ bar} + (\text{partial pressure of water vapor})$$

$$(\text{partial pressure of water vapor}) = 0.43 \text{ bar}$$

Let  $n$  be the number of moles of water vapor:

$$43000 \text{ Pa} \times 15.8 \text{ L} = n \times 8.31 \times 10^3 \times 360.15 \text{ K}$$

$$n = 0.23 \text{ mol}$$

Therefore, the number of moles of liquid water is:

$$n_1 = 1.00 - 0.23 = 0.77 \text{ mol (h)}$$

After this point, evaporation proceeds until equilibrium is reached, i.e., when the partial pressure of water vapor reaches the saturation value of  $p_s(87^\circ\text{C}) = 0.62 \text{ bar}$ . Therefore:

$$62000 \text{ Pa} \times 15.8 \text{ L} = n \times 8.31 \times 10^3 \times 360.15 \text{ K}$$

$$n = 0.33 \text{ mol}$$

Therefore, the number of moles of liquid water is:

$$n_2 = 1.00 - 0.33 = 0.67 \text{ mol (i)}.$$

### Problem 3. Molecules meet water and metals

1-1. The density of seawater is  $1.02 \text{ [g cm}^{-3}] = 1.02 \times 10^{-3} \text{ [kg cm}^{-3}] \times 10^6 \text{ [cm}^3 \text{ m}^{-3}] = 1.02 \times 10^3 \text{ [kg m}^{-3}]$ . The mass of a seawater column with a height of 20 m and a horizontal area of  $1 \text{ m}^2$  is  $1 \times 20 \text{ [m]} \times 1.02 \times 10^3 \text{ [kg m}^{-3}] = 2.04 \times 10^4 \text{ [kg m}^{-2}]$ . Thus, the pressure exerted by this seawater column on the  $1 \text{ m}^2$  bottom surface is  $2.04 \times 10^4 \times 9.81 \text{ N m}^{-2} [= \text{Pa}] = 2.00 \text{ bar}$ . Adding the atmospheric pressure of 1.01 bar to this pressure, we obtain a total pressure of 3.01 bar.

1-2. According to Henry's law, the mole fraction of nitrogen dissolved at 3.00 bar is  $3.00/(8.57 \times 10^4) = 3.50 \times 10^{-5}$ . The amount of water molecules in 5 L of water is  $5 \text{ [kg]}/18 \text{ [g mol}^{-1}] = 0.278 \times 10^3 \text{ mol}$ . Thus, the amount of dissolved nitrogen is  $0.278 \times 10^3 \times 3.50 \times 10^{-5} = 9.73 \times 10^{-3} \text{ mol}$ .

1-3. The amount of nitrogen dissolved in water at  $P = 0.800 \text{ bar}$  is  $0.8/(8.57 \times 10^4) \times 0.278 \times 10^3 = 2.60 \times 10^{-3} \text{ mol}$ . Thus, the volume of nitrogen gas is  $V = (9.73 \times 10^{-3} - 2.60 \times 10^{-3}) \times 8.31 \times 298.15 / (0.8 \times 10^5) = 2.21 \times 10^{-4} \text{ m}^3 = 0.221 \text{ [L]}$ .

2-1. Let  $n_l \text{ [mol]}$  be the amount of  $\text{CO}_2$  molecules dissolved in the water,  $n_g \text{ [mol]}$  be amount of  $\text{CO}_2$  molecules in the gas phase, and  $n_w (= V_l[L] \times \frac{1000}{18}) \text{ [mol]}$  be the amount of water molecules.

The mole fraction of  $\text{CO}_2$  can be estimated as  $x = n_l/n_w$  because  $n_w \gg n_l$ .

We thus obtain the following equations:

According to Henry's law,  $P = k_H x = k_H n_l/n_w$ ; thus,  $n_l = P n_w/k_H$  (1).

From the equation of the state of the gaseous part,  $P(V - V_l) = n_g RT$ :

$$n_g = P(V - V_l)/RT \quad (2)$$

The equation of the state for the gas initially added to the container:

$$n_0 = P_0(V - V_l)/RT \quad (3)$$

Conservation of the amount of  $\text{CO}_2$  at the initial and equilibrated conditions gives:

$$n_0 = n_g + n_l \quad (4)$$

Substituting equations (1)–(3) into equation (4) furnishes:

$$P = n_0 / (\alpha + \beta), \quad n_l = \beta P \quad ,$$

where

$$\alpha = \frac{V - V_l}{RT} (= 3.014 \times 10^{-3}), \quad \beta = \frac{n_w}{k_H} (= 2.671 \times 10^{-2}).$$

Thus,  $P = 5.07 \text{ atm}$  and  $n_l = 0.135 \text{ mol}$ .

2-2. The volume of  $\text{CO}_2$  dissolved in 0.5 L of water at  $0 \text{ }^\circ\text{C}$  under 1 atm is  $V = 0.135 \times 0.08201 \times 273.15 / 1.0 = 3.03 \text{ L}$ . Thus, 6.06 L of  $\text{CO}_2$  is dissolved in 1 L of water. Therefore, this solution is 6 GV carbonated water.

2-3. Following the same procedure as in Q2-1, we obtain  $P = 12.1 \text{ atm}$  and  $n_l = 0.119 \text{ mol}$  at  $50 \text{ }^\circ\text{C}$ .

3-1. Using similar equations to those for Q2-1 with respect to oxygen at its partial pressure of 0.21 bar, the mole fraction of dissolved oxygen is calculated to be  $4.8 \times 10^{-6}$  and the mass is 8.4 mg.

3-2. Let  $M^{(j)}$  be the quantities ( $M$ ) after replacing the atmosphere with pure argon  $j$  times.

The equation of the state for the gas phase part affords:

$$(P_A + P_O)(V - V_l) = (n_{O:g} + n_{A:g})RT$$

Henry's law for each gas:  $P_A = k_{H:A} x_A = \frac{n_A}{\beta_A}$ ,  $P_O = k_{H:O} x_O = \frac{n_O}{\beta_O}$ ,

where  $n_{i:g}$  and  $n_{i:l}$  ( $i = \text{A or O}$ ) are the amount of chemical species  $i$  in the gas phase and in

water, respectively, while  $n_W$  is the amount of water and  $\beta_i = \frac{n_W}{k_i}$ .

Conservation of the amount of oxygen before Ar replacement ( $j = 0$ ) gives:

$$n_O^{(0)} = n_{O:g}^{(0)} + n_{O:l}^{(0)}, \text{ where } n_{O:l}^{(0)} = \beta_O P_O^{(0)} = 2.64 \times 10^{-4} \text{ mol.}$$

After the first Ar replacement ( $j = 1$ ):

$$P_O^{(1)}(V - V_l) = n_{O:g}^{(1)}RT \text{ leads to } n_{O:g}^{(1)} = \alpha P_O^{(1)} \text{ and } n_{O:l}^{(1)} = \beta_O P_O^{(1)},$$

where  $\alpha = (V - V_l)/RT$ .

Because the oxygen dissolved in water before the replacement is distributed between the gas phase and water after the replacement, we obtain the relationship:

$$n_{O:l}^{(0)} = n_{O:g}^{(1)} + n_{O:l}^{(1)} = (\alpha + \beta_O)P_O^{(1)}$$

leading to  $P_O^{(1)} = \frac{n_{O:l}^{(0)}}{\alpha + \beta_O} = 6.35 \times 10^{-3}$  [bar]. Thus, the oxygen dissolved in the water after the Ar replacement is:

$$n_{O:l}^{(1)} = \beta_O P_O^{(1)} = \gamma n_{O:l}^{(0)} \text{ [mol], where } \gamma = \frac{\beta_O}{\alpha + \beta_O} = 3.02 \times 10^{-2}$$

Consequently:  $x_O^{(1)} = \frac{n_{O:l}^{(1)}}{n_W} = 1.4 \times 10^{-7}$ .

3-3. As found in Q3-2, the mole fraction of oxygen decreases by a factor of  $\gamma$  with each argon replacement. Here,  $\gamma = 3.02 \times 10^{-2}$ . Thus, the mole fraction of oxygen is  $4.3 \times 10^{-9}$  (after the second substitution),  $1.3 \times 10^{-10}$  (3rd),  $4.0 \times 10^{-12}$  (4th),  $1.2 \times 10^{-13}$  (5th). Therefore, 5 replacements are required to reduce the dissolved oxygen to 1 ppt or less.

4-1. The amounts of A and B are conserved before and after equilibrium:

$$n_A^0 = n_{A:l} + n_{A:g} + n_{AB;l} \quad (1)$$

$$n_B^0 = n_{B:l} + n_{B:g} + n_{AB;l} \quad (2)$$

The equations of state for the gases give:

$$n_A^0 = \alpha P_A^0, \quad n_B^0 = \alpha P_B^0, \quad (3)$$

$$n_{A:g} = \alpha P_A, \quad n_{B:g} = \alpha P_B \quad (4), \text{ where } \alpha = (V - V_l)/RT.$$

According to Henry's law,

$$n_{A:l} = \beta_A P_A, \quad n_{B:l} = \beta_B P_B \quad (5)$$

where  $\beta_i = \frac{n_W}{k_{H,i}}$  ( $i = A, B$ ).

$$\text{From } K_{AB} = x_{AB}/x_A x_B, \quad n_{AB} = K_{AB} \beta_A \beta_B P_A P_B / n_W, \quad (6)$$

where  $n_W$  is the amount of water.

Substituting equations (3)–(6) into equations (1) and (2), we obtain:

$$\alpha P_A^0 = (\alpha + \beta_A)P_A + K_{AB} \beta_A \beta_B P_A P_B / n_W \quad (7)$$

$$\alpha P_B^0 = (\alpha + \beta_B)P_B + K_{AB} \beta_A \beta_B P_A P_B / n_W \quad (8)$$

Solving the simultaneous equations with respect to  $P_A$  and  $P_B$ , we obtain:

$$P_A = 1.75, P_B = 1.86 \text{ [bar]},$$

$$x_A = 1.75 \times 10^{-4}, x_B = 9.30 \times 10^{-5}.$$

4-2. Similarly, the mole fraction of B is calculated to be  $x_B = 9.10 \times 10^{-5}$  at  $P_A^0 = 10$  bar and  $P_B^0 = 2$  bar. Thus, this is 97.8% of the mole fraction of B in Q4-1.

5-1. Adsorption rate :  $r_a = k_a PS$ , desorption rate:  $r_d = k_d a$

5-2. Because  $r_a = r_d$  at equilibrium:

$$k_a PS = k_d a.$$

Thus:

$$\frac{a}{PS} = \frac{k_a}{k_d} = K$$

Dividing each side of the equation by  $S_0$  and using  $S = S_0 - a$  and  $\theta = a/S_0$ , we obtain:

$$\theta = \frac{KP}{1 + KP}$$

5-3. Solving the above equation for  $P$ , we obtain:

$$P = \frac{\theta}{K(1-\theta)}.$$

In the case of  $\theta \ll 1$ ,  $P$  can be approximated as:

$$P = \theta/K.$$

5-4. The total amount  $n_t$  of gas molecules introduced into the container is given as:

$$n_t = \frac{P_0 V}{RT}$$

At equilibrium, the number of molecules in the gas phase ( $n_g$ ) and the number of molecules adsorbed on the metal surface ( $n_a$ ) are  $n_g = \frac{PV}{RT}$  and  $n_a = \theta S_0 A m$ , respectively.

As the total number of molecules is conserved before and after equilibrium:

$$n_t = n_g + n_a$$

From these equations, we obtain  $P = 58.7$  Pa and  $\theta = 0.998$ .

6-1. Similarly to Q5, we obtain:

$$\frac{a}{P_A S} = \frac{k_a^A}{k_d^A} = K_A \quad \frac{b}{P_B S} = \frac{k_a^B}{k_d^B} = K_B$$

Using  $S = S_0 - a - b$ , we obtain:

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \quad (1)$$

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \quad (2)$$

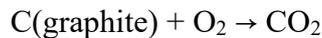
6-2. Using expressions (1) and (2), we obtain  $\theta_A = 0.538$  and  $\theta_B = 0.462$ .

6-3.  $\theta_A = K_A P_A$ ,  $\theta_B = K_B P_B$

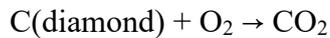
6-4. When  $P_B = 60.0$  Pa,  $\theta_A = 0.368$ , thus, it is 68.4% of the coverage  $\theta_A$  at  $P_B = 30.0$  Pa.

Problem 4. Synthesis of diamonds

1.



$$\Delta_c H^\circ(\text{graphite}) = -393.5 \text{ kJ mol}^{-1}$$



$$\Delta_c H^\circ(\text{diamond}) = -395.3 \text{ kJ mol}^{-1}$$

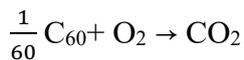
Therefore,



$$\Delta H = +1.8 \text{ kJ mol}^{-1}$$

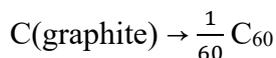
For the reaction above, the change in entropy is  $\Delta S = -3.25 \text{ J K}^{-1} \text{ mol}^{-1}$ .

$$\Delta G = \Delta H - T\Delta S = +2.77 \text{ kJ mol}^{-1}$$



$$\Delta_c H^\circ(\text{C}_{60}) = -\frac{25965}{60} = -432.8 \text{ kJ mol}^{-1}$$

Therefore,



$$\Delta H = +39.3 \text{ kJ mol}^{-1}$$

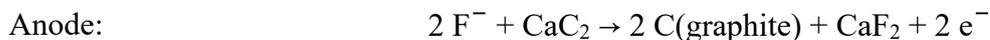
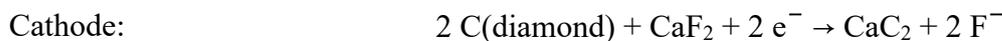
For the reaction above, the change in entropy is  $\Delta S = +1.54 \text{ J K}^{-1} \text{ mol}^{-1}$ .

$$\Delta G = \Delta H - T\Delta S = +38.8 \text{ kJ mol}^{-1}$$

The order of stability is thus graphite > diamond > C<sub>60</sub>.

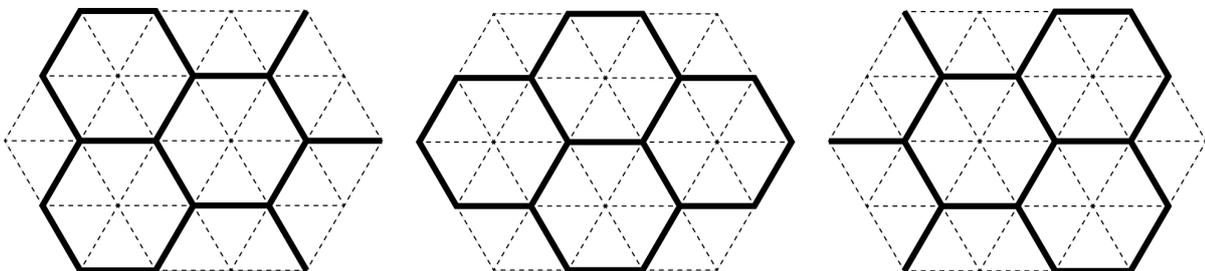
2. The reaction rate is very slow due to the high activation energy.

3.



4. The change in Gibbs free energy of the conversion reaction from diamond to graphite is  $\Delta G = -nFE = -1100 - 4.64T$  ( $n$  is the number of moles of electrons transferred per 1 mole of carbon, which is  $n = 1$  in this case). The thermodynamic quantities for the conversion reaction of graphite to diamond are obtained by changing the sign. By comparing the result with  $\Delta G = \Delta H - T\Delta S$ , the enthalpy and entropy are found to be  $\Delta H = +1.10 \text{ kJ mol}^{-1}$  and  $\Delta S = -4.64 \text{ J K}^{-1} \text{ mol}^{-1}$ .

5.



6. Left: 3R, center: 2H, right: 1H.

7. Left: lonsdaleite, right: diamond.

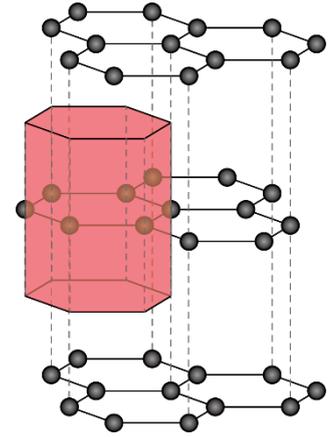
8. The area of the hexagonal cell that constitutes graphene is

$$1.42 \times (1.42 \times \sin 60^\circ) \times \frac{1}{2} \times 6 = 5.24 \text{ \AA}^2.$$

The number of carbon atoms within this hexagonal cell is two.

Based on these values, the volume occupied by two carbon atoms (see the right figure) can be calculated as  $5.24 \times 3.35 = 17.55 \text{ \AA}^3$ .

Therefore, the density of graphite is  $\frac{12.01 \times 2 / 6.02 \times 10^{23}}{17.55 \times 10^{-24}} = 2.27 \text{ g cm}^{-3}$ .



The side length of the unit cell of a diamond is  $4/\sqrt{3}$  times the distance between covalently bonded carbon atoms, which can be calculated to be  $3.56 \text{ \AA}$ .

There are eight carbon atoms in the unit cell.

Based on these values, the volume occupied by eight carbon atoms can be calculated as  $3.56^3 = 44.98 \text{ \AA}^3$ .

Therefore, the density of diamond is  $\frac{12.01 \times 8 / 6.02 \times 10^{23}}{44.98 \times 10^{-24}} = 3.55 \text{ g cm}^{-3}$ .

9. If there is no volume change between graphite and diamond, the density of graphite and diamond should be the same. Using the results of question 8, the distance between layers can be calculated as  $3.35 \times \frac{2.27}{3.55} = 2.14 \text{ \AA}$ .

The distance between graphene layers is estimated to be as large as  $2.78 \text{ \AA}$  even under 30 GPa (300,000 bar). Therefore, the direct conversion method requires high temperature in addition to high pressure to accelerate the reaction.

10.  $v_g = v'_g \rightarrow k_g C_C = k'_g C_H, C_h = \frac{k_g}{k'_g} C_C$

11.  $v_d - v'_d = v_d - k'_d \frac{k_g}{k'_g} C_C = v_d \left( 1 - \frac{k'_d k_g}{k_d k'_g} \right)$

Based on this result, the conditions that the reaction constants should satisfy is given by  $\frac{k'_d k_g}{k_d k'_g} < 1$ .

12. Let the growth rate of the diamond be  $r_c$ . (From here on, we assume that  $r$  and  $A$  are non-dimensional normalized by the unit  $\mu\text{m h}^{-1}$ .)

$$r_c = A_{c,13\%} \exp\left(-\frac{E_a^c}{RT}\right) \rightarrow \ln r_c = \ln A_{c,13\%} - \frac{E_a^c}{RT}$$

Substituting in the experimental results gives:

$$\ln 30.34 = \ln A_{c,13\%} - \frac{E_a^c}{1173.15R}$$

$$\ln 63.43 = \ln A_{c,13\%} - \frac{E_a^c}{1373.15R}$$

From these equations, the value  $E_a^c = 49.4 \text{ kJ mol}^{-1}$  is obtained.

13. Let the etching rate of the diamond be  $r_h (> 0)$ :

$$r_h = A_h \exp\left(-\frac{E_a^h}{RT}\right) \rightarrow \ln r_h = \ln A_h - \frac{E_a^h}{RT}$$

Substituting in the experimental results gives:

$$\ln 1.58 = \ln A_h - \frac{E_a^h}{1173.15R}$$

$$\ln 5.52 = \ln A_h - \frac{E_a^h}{1373.15R}$$

From these equations, the values  $A_h = 8486$  and  $E_a^h = 83.8 \text{ kJ mol}^{-1}$  are obtained.

14. At 1000 °C, the condition  $r_c = r_h$  is fulfilled.

$$\ln A_{c,1\%} - \frac{E_a^c}{1273.15R} = \ln A_h - \frac{E_a^h}{1273.15R}$$

From this equation, the value  $A_{c,1\%} = 330$  is obtained.

The condition that must be satisfied can be expressed as follows:

$$A_{c,1\%} \exp\left(-\frac{E_a^c}{RT}\right) - A_h \exp\left(-\frac{E_a^h}{RT}\right) = 0.50$$

By substituting in the calculated values above and calculating the left-hand side of the above equation with different  $T$  values,  $T = 900 \text{ °C}$  is obtained.

Problem 5. Count the number of states

1.

$$W(40,60) = {}_{100}C_{40} = \frac{100!}{40! 60!}$$

Using the approximate formula:

$$\begin{aligned} 100! &\approx 9.4 \times 10^{157} \\ 40! &\approx 8.2 \times 10^{47} \\ 60! &\approx 8.4 \times 10^{81} \end{aligned}$$

we obtain  $W(40,60) = 1.4 \times 10^{28}$ . Similarly:

$$W(50,50) = {}_{100}C_{50} = \frac{100!}{50! 50!} = \frac{9.4 \times 10^{157}}{(3.1 \times 10^{64})^2} = 9.9 \times 10^{28}$$

2. As the number of states is maximized when an equal number of molecules is present in each of the two chambers A and B,  $n^* = 5$  and 50, *i.e.*, the arrangements (5,5) and (50,50) are most probable for  $N = 10$  and  $N = 100$ , respectively.

Given that each molecule has two possible locations, *i.e.*, in either of the two chambers, the total number of possible arrangements of  $N$  molecules is  $2^N$ . Thus, the probability of the occurrence of the arrangement (n, m) is given by  $P(n,m) = W(n,m)/2^N$ . Consequently:

$$P(5,5) = W(5,5)/2^{10} = 252/1024 = 0.246$$

$$P(50,50) = W(50,50)/2^{100} = 1.012 \times 10^{29}/1.267 \times 10^{30} = 0.0799$$

In the case of  $N = 10$ , only the arrangement (5,5) falls within the specified range. In the case of  $N = 100$ , the following 5 arrangements are within this range: (48,52), (49,51), (50,50), (51,49), (52,48).

The numbers of states for each arrangement are:

$$\begin{aligned} W(48,52) &= W(52,48) = 9.34404 \times 10^{28} \\ W(49,51) &= W(51,49) = 9.91608 \times 10^{28} \\ W(50,50) &= 1.01144 \times 10^{29} \end{aligned}$$

Thus, we obtain:

$$\begin{aligned} P(48,52) &= P(52,48) = 0.0737 \\ P(49,51) &= P(51,49) = 0.0782 \\ P(50,50) &= 0.0798 \end{aligned}$$

Therefore:

$$P_{total} = (0.0737 + 0.0782) \times 2 + 0.0798 = 0.384$$

This indicates that the probability of finding a state in the given  $n^*$  range is larger for  $N = 100$  than for  $N = 10$ .

3. Using the analogy of one molecule in the container:

$$\frac{W_{AB}}{W_A} = \left(\frac{V_2}{V_1}\right)^{nN_A}$$

when  $n$  moles of molecules are present in the container, where  $N_A$  is the Avogadro constant.

Thus:

$$\Delta S = S_2 - S_1 = k_B \ln W_{AB} - k_B \ln W_A = k_B \ln \frac{W_{AB}}{W_A} = nR \ln \frac{V_2}{V_1}$$

4.

$$\Delta S = 0.30 \times 8.3 \times \ln \frac{0.40}{0.10} = 3.5 \text{ [J K}^{-1}\text{]}$$

5. The temperature, number of molecules, and volume do not change from State 1 to State 2. Thus, the entropy of the system does not change.

$$\Delta S = 0$$

6. According to the equation derived in question 3, the entropy changes upon the expansion of gases of  $\alpha$  and  $\beta$  is given by:

$$\Delta S = n_{\alpha} R \ln \frac{V_A + V_B}{V_A} + n_{\beta} R \ln \frac{V_A + V_B}{V_B}$$

The volume ratios can be replaced by the ratios of the amounts of gas molecules to give:

$$\frac{V_A}{V_A + V_B} = \frac{n_{\alpha}}{n_{\alpha} + n_{\beta}}$$

$$\frac{V_B}{V_A + V_B} = \frac{n_{\beta}}{n_{\alpha} + n_{\beta}}$$

Thus:

$$\Delta S = -R \left( n_{\alpha} \ln \frac{n_{\alpha}}{n_{\alpha} + n_{\beta}} + n_{\beta} \ln \frac{n_{\beta}}{n_{\alpha} + n_{\beta}} \right)$$

7. As both chambers are filled with identical molecules of type  $\alpha$ , we cannot distinguish whether a molecule was originally present in chamber A or B after mixing. Furthermore, because the pressure is kept constant, there is no entropy change by removing the boundary wall. Therefore, the entropy does not change from State 1 to State 2.

$$\Delta S = 0$$

8. Given that a  $\text{H}_3\text{CD}$  molecule in a crystal has four different orientations, the molar residual entropy is given by:

$$S = R \ln 4 = 11.5 \text{ [J K}^{-1} \text{ mol}^{-1}\text{]}$$

- 9-1. Along the O–O axis of two adjacent oxygen atoms there are two stable positions for a hydrogen atom, and each water molecule possesses two hydrogen atoms. Thus, the number of configurations for the hydrogen atoms of one water molecule without the constraints of the ice rules is  $2^2 = 4$ . Thus, the number of configurations for 1 mole of water is  $(2^2)^{N_A}$ .

9-2.  $2^2 \times 4 = 16$

9-3.

$$(\text{H}_4\text{O})^{2+} : W = 1$$

$$(\text{H}_3\text{O})^+ : W = 4$$

$$(\text{OH})^- : W = 4$$

$$\text{O}^{2-} : W = 1$$

Thus, the number of configurations satisfying the ice rules is  $16 - 10 = 6$ .

- 9-4. The number of configurations satisfying the ice rules in an ice crystal with one mole of water can be calculated by:

$$W = (2^2)^{N_A} \left( \frac{6}{16} \right)^{N_A} = \left( \frac{3}{2} \right)^{N_A}$$

Thus, the molar residual entropy is given by:

$$S = k_B \ln W = R \ln \frac{3}{2} = 3.37 \text{ [J K}^{-1} \text{ mol}^{-1}\text{]}$$

Problem 6. The path of chemical reactions

1.

$$T = \frac{1}{2}m_A\mathbf{v}_A^2 + \frac{1}{2}m_B\mathbf{v}_B^2 = \frac{1}{2}m_A\mathbf{v}_A^2 + \frac{1}{2}m_B\mathbf{v}_B^2 - \frac{1}{2}\mu(\mathbf{v}_A - \mathbf{v}_B)^2 + \frac{1}{2}\mu(\mathbf{v}_A - \mathbf{v}_B)^2$$

To summarize 1–3 items in the equation

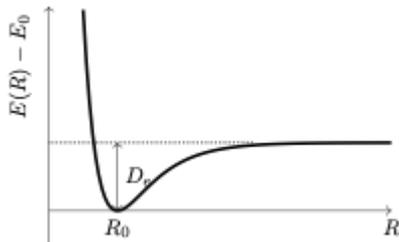
$$\begin{aligned} \frac{1}{2}m_A\mathbf{v}_A^2 + \frac{1}{2}m_B\mathbf{v}_B^2 - \frac{1}{2}\left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{-1}(\mathbf{v}_A - \mathbf{v}_B)^2 &= \frac{1}{2}m_A\mathbf{v}_A^2 + \frac{1}{2}m_B\mathbf{v}_B^2 - \frac{1}{2}\frac{m_A m_B}{m_A + m_B}(\mathbf{v}_A - \mathbf{v}_B)^2 \\ &= \frac{1}{2(m_A + m_B)}\{m_A(m_A + m_B)\mathbf{v}_A^2 + m_B(m_A + m_B)\mathbf{v}_B^2 - m_A m_B(\mathbf{v}_A - \mathbf{v}_B)^2\} \\ &= \frac{1}{2(m_A + m_B)}\{m_A^2\mathbf{v}_A^2 + m_B^2\mathbf{v}_B^2 + 2m_A m_B\mathbf{v}_A\mathbf{v}_B\} = \frac{1}{2(m_A + m_B)}(m_A\mathbf{v}_A + m_B\mathbf{v}_B)^2 \\ &= \frac{m_A + m_B}{2}\left(\frac{m_A\mathbf{v}_A + m_B\mathbf{v}_B}{m_A + m_B}\right)^2 \equiv \frac{1}{2}M_1\mathbf{v}_1^2 \end{aligned}$$

Thus

$$\begin{aligned} M_1 &= m_A + m_B \\ \mathbf{v}_1 &= \frac{m_A\mathbf{v}_A + m_B\mathbf{v}_B}{m_A + m_B} \end{aligned}$$

2.  $k^S < k^D$  and  $R^{S_0} > R^{D_0}$

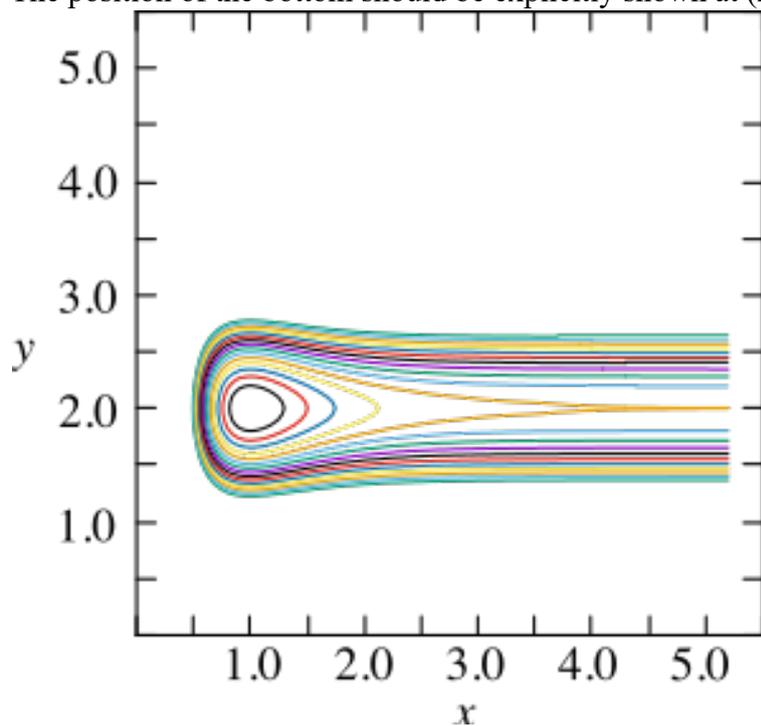
3.



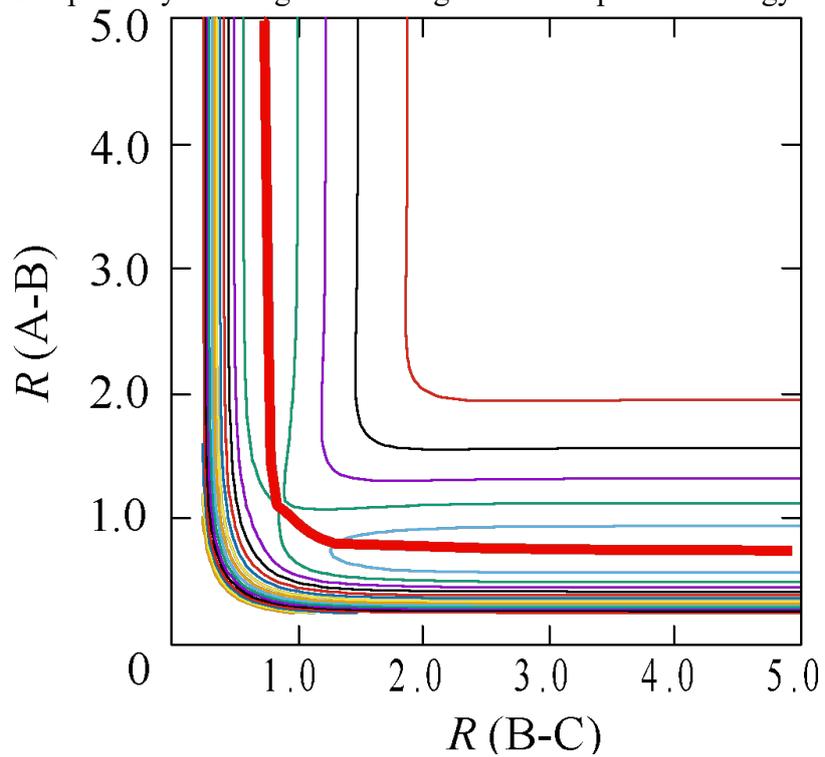
4.

- 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.

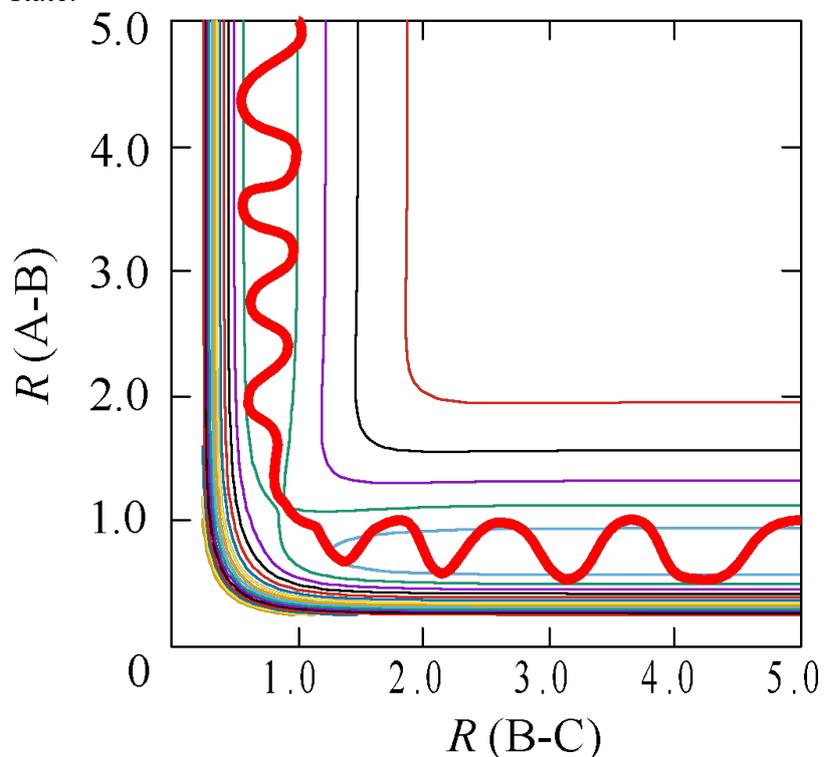
5. The position of the bottom should be explicitly shown at  $(x,y)=(1,2)$ .



6. The pathway is a single line along the lowest point of energy.



7. The pathway is a single line, oscillating in a direction normal to the progress of the reaction (when the reaction goes the vertical direction, the oscillation occurs horizontally or vice versa). Details of the amplitude and phase are not so important, but the amplitude is the narrowest in the transition state.



8. A:  $R_{CM}$ , B:  $R_{CH}$ , C:  $R_{CC}$ , D:  $R_{HF}$

## Problem 7. Molecular vibrations and infrared spectroscopy

1. Given that the spring constant is identical in both compounds,  $\nu_{DF}$  can be calculated by:

$$\nu_{DF} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_{DF}}} \text{ with a reduced mass of } \mu_{DF} = \frac{m_D m_F}{m_D + m_F}.$$

As the wavenumber,  $\tilde{\nu}$ , is related to the frequency,  $\nu$ , via  $\nu = c\tilde{\nu}$  ( $c$ : velocity of light):

$$\tilde{\nu}_{DF} = \tilde{\nu}_{HF} \sqrt{\frac{\mu_{HF}}{\mu_{DF}}} \text{ is obtained } (\tilde{\nu}_{HF} = 3953.8 \text{ cm}^{-1}).$$

Consequently, we can reach the conclusion:  $\tilde{\nu}_{DF} = \underline{2866 \text{ cm}^{-1}}$ .

(cf. experimentally observed position:  $2896 \text{ cm}^{-1}$ )

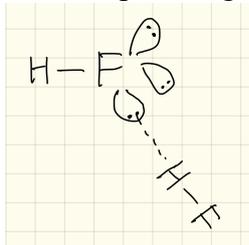
- 2.

$$q_{\text{vib}} = \sum_{v=0}^{\infty} \exp\left(-\frac{E_v}{k_B T}\right) = \exp\left(-\frac{h\nu}{2k_B T}\right) \sum_{v=0}^{\infty} \exp\left(-\frac{v h\nu}{k_B T}\right) = \frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} = \frac{\exp\left(-\frac{\theta}{2T}\right)}{1 - \exp\left(-\frac{\theta}{T}\right)}$$

3. When calculating the frequency in wavenumbers using  $\tilde{\nu} = 1/\lambda$ , take care regarding the unit conversion, especially for  $\text{cm}^{-1}$ .

$$\theta = \frac{h\nu}{k_B} = \frac{hc\tilde{\nu}}{k_B} = \underline{5689 \text{ K}}$$

4. A bent structure as depicted below should be drawn, because the fluorine atom has three lone pairs with an  $sp^3$  configuration.



L. Andrews and G.L. Johnson, *J. Phys. Chem.* **88**, 425 (1984).

5. (2)  $k$  becomes smaller and  $m$  becomes larger, which results in a shift to a lower wavenumber.
6. The wavenumber, where a peak appears in an IR spectrum corresponds to the energy gap between the two levels,  $h\nu$ , which can directly be used as  $\Delta E$  in the Boltzmann factor.

$$\frac{g_1}{g_0} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{h\nu}{k_B T}\right) = \exp\left(-\frac{hc\tilde{\nu}}{k_B T}\right)$$

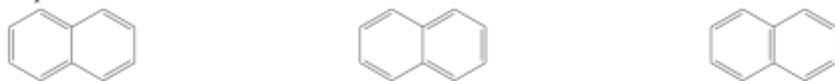
$$\text{At 12 K: } g_1/g_0 = \underline{1.327 \times 10^{-206}}$$

$$\text{At 25 } ^\circ\text{C: } g_1/g_0 = \underline{5.174 \times 10^{-9}}$$

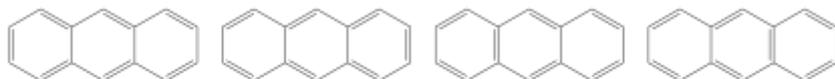
Problem 8. Quantum chemistry of aromatic molecules

1.

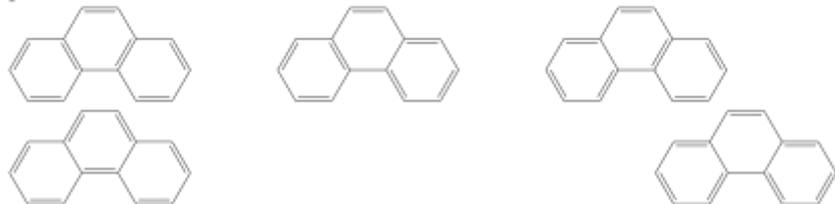
(a) naphthalene



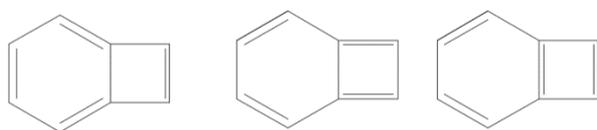
(b) anthracene



(c) phenanthrene



(d)



2. In anthracene, the resonance structure shows that the fraction of double-bond character for each of the bonds is  $R_3 = 3/4$ ,  $R_1 = 1/2$ , and  $R_2 = 1/4$ .

$$R_D (1.34) < R_3 (1.356) < R_1 (1.410) < R_2 (1.430) < R_S (1.53)$$

3. benzene: 3; naphthalene: 5; pyrrole: 3

4. (c)

5. (a), (c), (b)

Problem 9. Protic ionic liquids



1-2.  $[\text{CH}_3\text{OH}_2^+] = [\text{CH}_3\text{O}^-] = (10^{-16.7})^{1/2} = 4 \times 10^{-9} \text{ mol L}^{-1}$

2-1.

$$C_H = [\text{HB}]_0 \frac{V_0}{V_0 + V_i} + [\text{CH}^+]_{\text{sol}}$$

$$C_{\text{im}} = [\text{C}]_0 \frac{V_i}{V_0 + V_i} + [\text{CH}^+]_{\text{sol}}$$

2-2.

$$E_i = E^\circ + \frac{RT}{F} \ln [\text{HB}] = E^\circ + \frac{RT}{F} \ln \frac{[\text{HB}]_0 V_0 - [\text{C}]_0 V_i}{V_0 + V_i}$$

Based on the above equation and the numerical values provided:

$$E^\circ = 0.796 - \frac{8.314 \cdot 298.15}{96485} \ln \frac{0.35 \cdot 7.3 \times 10^{-3} - 3.2 \cdot 0.5 \times 10^{-3}}{(7.3 + 0.5) \times 10^{-3}} = 0.85 \text{ V}$$

3-1.  $[\text{HB}] = K_s / [\text{C}]$

By using the approximation  $C_H \approx [\text{CH}^+]$ ,

$$[\text{C}] = C_{\text{im}} - [\text{CH}^+] = C_{\text{im}} - C_H$$

From these equations:  $[\text{HB}] = K_s / (C_{\text{im}} - C_H)$

3-2.

$$E_i = E^\circ + \frac{RT}{F} \ln [\text{HB}] = E^\circ + \frac{RT}{F} \ln \frac{K_s}{C_{\text{im}} - C_H}$$

This equation can be rearranged into the following form (Gran's plot):

$$\frac{(E_i - E^\circ)F}{RT} = \ln \frac{K_s(V_0 + V_i)}{[\text{C}]_0 V_i - [\text{HB}]_0 V_0} \rightarrow \exp \left[ \frac{E_i F}{RT} \right] = \exp \left[ \frac{E^\circ F}{RT} \right] \frac{K_s(V_0 + V_i)}{[\text{C}]_0 V_i - [\text{HB}]_0 V_0}$$

$$\rightarrow (V_0 + V_i) \exp \left[ -\frac{E_i F}{RT} \right] = \exp \left[ -\frac{E^\circ F}{RT} \right] \frac{[\text{C}]_0 V_i - [\text{HB}]_0 V_0}{K_s}$$

By substituting in the numerical values,  $K_s = 5.1 \times 10^{-13} \text{ mol}^2 \text{ L}^{-2}$  is obtained.

$$\exp \left[ -\frac{E^\circ F}{RT} \right] \frac{[\text{C}]_0}{K_s} = \exp \left[ -\frac{0.85 \cdot 96485}{8.314 \cdot 298.15} \right] \frac{3.2}{K_s} = 0.0271 \rightarrow K_s = 5.1 \times 10^{-13} \text{ mol}^2 \text{ L}^{-2}$$

4-1. When  $\text{pH} = 9.27 (= \text{p}K_a)$ ,  $f_a = 0.50$ .

$$1/2 = 1 - \exp(-0.50 k' t)$$

By solving the equation for  $t$ :  $t = 28 \text{ s}$ .

4-2.  $1/3 = 1 - \exp(-f_a k' 500)$

By solving the equation for  $f_a$ :  $f_a = 1.62 \times 10^{-2}$ .

$$K_a = \frac{[\text{R}^1 - \text{NH}_2][\text{H}_3\text{O}^+]}{[\text{R}^1 - \text{NH}_3^+]} \approx f_a [\text{H}_3\text{O}^+] = 10^{-9.27}$$

By solving the equation for  $[\text{H}_3\text{O}^+]$ :  $[\text{H}_3\text{O}^+] = 3.26 \times 10^{-8}$  and  $\text{pH} = 7.49$ .

[Note] Proof of eq. 12 (for mentors only, students do not have to calculate by themselves):

$$\begin{aligned}\frac{d[\text{NHCO}]}{dt} &= ([\text{R}^1-\text{NH}_2]_0 + [\text{R}^1-\text{NH}_3^+]_0)k[\text{R}^2-\text{CO}-\text{NHS}]f_a \exp(-k[\text{R}^2-\text{CO}-\text{NHS}]f_a t) \\ &= [\text{R}^1-\text{NH}_2]_0 k[\text{R}^2-\text{CO}-\text{NHS}] \exp(-k[\text{R}^2-\text{CO}-\text{NHS}]f_a t) \\ &= k[\text{R}^1-\text{NH}_2][\text{R}^2-\text{CO}-\text{NHS}]\end{aligned}$$

Note that  $([\text{R}^1-\text{NH}_2]_0 + [\text{R}^1-\text{NH}_3^+]_0)f_a = [\text{R}^1-\text{NH}_2]_0$ .

5-1.

$$K_a^C = \frac{[\text{C}][\text{HB}]}{[\text{CH}^+]} = 10^{-14.90}$$

Let  $[\text{HB}] = x$ ,

$$\frac{x^2}{(6.00 \times 10^{-3} - x)} \approx \frac{x^2}{6.00 \times 10^{-3}} = 10^{-14.90}$$

By solving the equation for  $x$ :  $x = 2.75 \times 10^{-9} \text{ mol L}^{-1}$ .

5-2.  $[\text{R}^1-\text{NH}_2]_0$  is calculated to be  $10.00 \times 10^{-3} \text{ mol L}^{-1}$ .

$$K_a^A = \frac{[\text{R}^1-\text{NH}_2][\text{HB}]}{[\text{R}^1-\text{NH}_3^+]} = \frac{(10.00 \times 10^{-3} - [\text{R}^1-\text{NH}_3^+])[\text{HB}]}{[\text{R}^1-\text{NH}_3^+]} = 10^{-16.40}$$

By solving the equation for  $[\text{R}^1-\text{NH}_3^+]$  with  $[\text{HB}] = 5.39 \times 10^{-17} \text{ mol L}^{-1}$ ,  $[\text{R}^1-\text{NH}_3^+] = 5.75 \times 10^{-3} \text{ mol L}^{-1}$  is obtained.

$[\text{R}^1-\text{NH}_2] = 10.00 \times 10^{-3} \text{ mol L}^{-1} - [\text{R}^1-\text{NH}_3^+] = 4.25 \times 10^{-3} \text{ mol L}^{-1}$ .

$$K_a^C = \frac{[\text{C}][\text{HB}]}{[\text{CH}^+]} = \frac{(6.00 \times 10^{-3} - [\text{CH}^+])[\text{HB}]}{[\text{CH}^+]} = 10^{-14.90}$$

By solving the equation for  $[\text{CH}^+]$ ,  $[\text{CH}^+] = 2.46 \times 10^{-4} \text{ mol L}^{-1}$ .

$[\text{C}] = 6.00 \times 10^{-3} \text{ mol L}^{-1} - [\text{CH}^+] = 5.75 \times 10^{-3} \text{ mol L}^{-1}$ .

The result shows that  $[\text{C}] = [\text{R}^1-\text{NH}_3^+]$ , which means that all the protons dissociated from  $\text{CH}^+$  are transferred to  $\text{R}^1-\text{NH}_2$ .

5-3. Solve the following simultaneous equations. Note that  $2.00 \times 10^{-3} \text{ mol L}^{-1}$  of  $\text{R}^1-\text{NH}_2$  is consumed by the reaction between  $\text{R}^1-\text{NH}_2$  and  $\text{R}^2-\text{CO}-\text{NHS}$ , which generates  $2.00 \times 10^{-3} \text{ mol L}^{-1}$  of protons. Therefore, the total proton concentration becomes  $6.00 \times 10^{-3}$  (concentration of  $\text{CH}^+/\text{B}^-$  solution) +  $2.00 \times 10^{-3} = 8.00 \times 10^{-3} \text{ mol L}^{-1}$ .

$$K_a^A = \frac{[\text{R}^1-\text{NH}_2][\text{HB}]}{[\text{R}^1-\text{NH}_3^+]} = \frac{(8.00 \times 10^{-3} - [\text{R}^1-\text{NH}_3^+])[\text{HB}]}{[\text{R}^1-\text{NH}_3^+]} = 10^{-16.40} \quad (20)$$

$$K_a^C = \frac{[\text{C}][\text{HB}]}{[\text{CH}^+]} = \frac{(6.00 \times 10^{-3} - [\text{CH}^+])[\text{HB}]}{[\text{CH}^+]} = 10^{-14.90} \quad (21)$$

$$[\text{R}^1-\text{NH}_3^+] + [\text{CH}^+] + [\text{HB}] \approx [\text{R}^1-\text{NH}_3^+] + [\text{CH}^+] = 8.00 \times 10^{-3} \quad (22)$$

By substituting eq. 22 into eq. 21, the following is obtained:

$$[\text{R}^1-\text{NH}_3^+][\text{HB}] = 1.007 \times 10^{-17} - 10^{-14.9}[\text{R}^1-\text{NH}_3^+] + 2.00 \times 10^{-3}[\text{HB}] \quad (23)$$

By substituting eq. 23 into eq. 20, the following is obtained:

$$[\text{HB}] = 1.679 \times 10^{-15} - 2.032 \times 10^{-13}[\text{R}^1-\text{NH}_3^+] \quad (24)$$

By substituting eq. 24 into eq. 23, the following is obtained:

$$2.032 \times 10^{-13}[\text{R}^1-\text{NH}_3^+]^2 - 3.344 \times 10^{-15}[\text{R}^1-\text{NH}_3^+] + 1.343 \times 10^{-17} = 0 \quad (25)$$

By solving eq. 25,  $[\text{R}^1-\text{NH}_3^+] = 6.96 \times 10^{-3} \text{ mol L}^{-1}$  is obtained.

$[\text{R}^1-\text{NH}_2] = 8.00 \times 10^{-3} \text{ mol L}^{-1} - [\text{R}^1-\text{NH}_3^+] = 1.04 \times 10^{-3} \text{ mol L}^{-1}$ .

By substituting these values into eq. 20,  $[\text{HB}] = 2.65 \times 10^{-16} \text{ mol L}^{-1}$  is obtained.

By substituting these values into eq. 21,  $[\text{CH}^+] = 1.04 \times 10^{-3} \text{ mol L}^{-1}$  is obtained.  
 $[\text{C}] = 6.00 \times 10^{-3} \text{ mol L}^{-1} - [\text{CH}^+] = 4.96 \times 10^{-3} \text{ mol L}^{-1}$ .

The result shows that  $[\text{R}^1\text{-NH}_3^+] = [\text{C}] + 2.00 \times 10^{-3} \text{ mol L}^{-1}$ , which means that all the protons dissociated from  $\text{CH}^+$  and the protons generated by the reaction ( $2.00 \times 10^{-3} \text{ mol L}^{-1}$ ) are transferred to  $\text{R}^1\text{-NH}_2$ .

5-4. From eq. 18,  $[\text{HB}] = K_a^{\text{C}} [\text{CH}^+] / [\text{C}]$

(By rearranging the above equation, the Henderson–Hasselbalch equation is obtained:

$$\text{pH} = \text{p}K_a^{\text{C}} - \log([\text{CH}^+] / [\text{C}])$$

5-5.  $1/3 = 1 - \exp(-f_a k' 2000)$

By solving the equation for  $f_a$ :  $f_a = 0.253$ .

$$K_a^{\text{A}} = \frac{[\text{R}^1\text{-NH}_2][\text{HB}]}{[\text{R}^1\text{-NH}_3^+]} = \frac{0.253[\text{HB}]}{1 - 0.253} = 10^{-16.40}$$

By solving the equation for  $[\text{HB}]$ ,  $[\text{HB}] = 1.173 \times 10^{-16}$ .

From the equation of Q5-4,  $[\text{C}] / [\text{CH}^+] = 10.73$  and  $[\text{C}] = 1.07 \text{ mol L}^{-1}$  are obtained.

## Problem 10. The Yamada universal indicator

1-1. At pH = 2.00, only the protonated form is present. At pH = 12.00, only the deprotonated form is present. For example, the molar absorption coefficient of the protonated form at 420 nm can be calculated using the absorbance at pH = 2.00 as follows:

$$\varepsilon(420 \text{ nm}) \cdot 200 \times 10^{-6} \text{ mol L}^{-1} \cdot 1 \text{ cm} = 1.74 \rightarrow \varepsilon(420 \text{ nm}) = 8.7 \times 10^3 \text{ mol}^{-1} \text{ L cm}^{-1}$$

The other molar absorption coefficients are calculated in a similar way (unit: mol<sup>-1</sup> L cm<sup>-1</sup>).

Wavelength	420 nm	501 nm	520 nm
Protonated	$8.7 \times 10^3$	$3.5 \times 10^3$	$1.8 \times 10^3$
Deprotonated	$3.0 \times 10^3$	$3.5 \times 10^3$	$5.3 \times 10^3$

1-2. Let the concentration of the protonated form be  $x \text{ mol L}^{-1}$  and let that of the deprotonated form be  $y \text{ mol L}^{-1}$ . Using the conditions given in the problem, the following two equations are obtained:

$$8.7 \times 10^3 x + 3.0 \times 10^3 y = 1.13$$

$$1.8 \times 10^3 x + 5.3 \times 10^3 y = 0.52$$

By solving these equations, the values  $x = 1.09 \times 10^{-4}$  and  $y = 0.61 \times 10^{-4}$  are obtained. From the definition of the acid dissociation constant of BTB:

$$10^{-7.1} = [\text{H}^+] y/x, [\text{H}^+] = 1.41 \times 10^{-7} \text{ mol L}^{-1} \rightarrow \text{pH} = 6.85$$

1-3, 4.

The pH does not matter, because 501 nm corresponds to the isosbestic point of BTB. The concentration of the indicator of the solution used in Q1-2 is  $x + y = 1.70 \times 10^{-4} \text{ mol L}^{-1}$ . Therefore, the absorbance at 501 nm before dilution is 0.595. After the five-fold dilution, the absorbance is 0.119.

2. As examples, let us focus on the absorbance values that are highlighted in the following table:

	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

The concentrations of the indicators in the final solutions are as follows (unit: mol L<sup>-1</sup>):

Indicator	TB	MR	BTB	PP
Concentration	$3.572 \times 10^{-6}$	$1.547 \times 10^{-5}$	$2.669 \times 10^{-5}$	$1.047 \times 10^{-4}$

(1) The pH of the solution is estimated to be 3–6 because the color of the solution is yellow. In this pH region, it is reasonable to assume that all the TB and PP exist as HA<sup>-</sup>. Most of the BTB will exist as HA<sup>-</sup>, although there may be a small amount of A<sup>2-</sup>. Therefore, it is only necessary to focus on the HA<sup>-</sup>/A<sup>2-</sup> ratio of MR. In principle, we can calculate this ratio using any wavelength. Because the molar absorption coefficients of the HA<sup>-</sup> and A<sup>2-</sup> forms of BTB are the same at 500 nm, we can ignore the HA<sup>-</sup>/A<sup>2-</sup> ratio of BTB by using the absorbance at 500 nm. The contributions to the absorbance of the solution at 500 nm from TB, BTB, and PP are as follows:

$$\text{TB: } \varepsilon(\text{HA}^-, 500 \text{ nm}) = 3000, \text{ concentration: } 3.572 \times 10^{-6} \text{ mol L}^{-1} \rightarrow \text{Absorbance: } 0.011$$

$$\text{BTB: } \varepsilon(500 \text{ nm}) = 3500, \text{ concentration: } 2.669 \times 10^{-5} \text{ mol L}^{-1} \rightarrow \text{Absorbance: } 0.093$$

$$\text{PP: } \varepsilon(\text{HA}^-, 500 \text{ nm}) = 0, \text{ concentration: } 1.047 \times 10^{-4} \text{ mol L}^{-1} \rightarrow \text{Absorbance: } 0.000$$

From these results, the absorbance at 500 nm originating from MR can be calculated to be  $0.460 - 0.011 - 0.093 = 0.356$ .

By considering the concentration of the protonated form of MR,  $[\text{HA}^-]_{\text{MR}}$ , and that of the deprotonated form,  $[\text{A}^{2-}]_{\text{MR}}$ , which is  $1.547 \times 10^{-5} \text{ mol L}^{-1} - [\text{A}^{2-}]_{\text{MR}}$ , the following equation is obtained:

$$35000 [\text{HA}^-]_{\text{MR}} + 4000 (1.547 \times 10^{-5} - [\text{HA}^-]_{\text{MR}}) = 0.356$$

By solving the above equation, the values  $[\text{HA}^-]_{\text{MR}} = 9.49 \times 10^{-6} \text{ mol L}^{-1}$  and  $[\text{A}^{2-}]_{\text{MR}} = 5.98 \times 10^{-6} \text{ mol L}^{-1}$  are obtained.

By substituting these results into the definition of the acid dissociation constant of MR:

$$10^{-5.1} = [\text{H}^+] [\text{A}^{2-}]_{\text{MR}} / [\text{HA}^-]_{\text{MR}} \rightarrow [\text{H}^+] = 1.26 \times 10^{-5} \text{ mol L}^{-1}, \text{pH} = 4.9$$

- (2) The pH of the solution is estimated to be 6–8 because the color of the solution is green. In this pH region, it is reasonable to assume that all the PP exists as  $\text{HA}^-$ . However, it is difficult to estimate the ratios of the protonated forms of the other indicators in this pH region. From Table 4, we can see that the absorbance at 650 nm is governed by the deprotonated form of BTB. Although the  $\text{A}^{2-}$  form of TB also contributes to the absorption, this contribution will be negligible because the concentration of TB is one order of magnitude smaller than that of BTB.

The following equation is then obtained for the concentration of the deprotonated form of BTB,  $[\text{A}^{2-}]_{\text{BTB}}$ :

$$10000 [\text{A}^{2-}]_{\text{BTB}} = 0.089$$

By solving the above equation, the values  $[\text{A}^{2-}]_{\text{BTB}} = 8.9 \times 10^{-6} \text{ mol L}^{-1}$  and  $[\text{HA}^-]_{\text{BTB}} = 2.669 \times 10^{-5} \text{ mol L}^{-1} - [\text{A}^{2-}]_{\text{BTB}} = 1.78 \times 10^{-5} \text{ mol L}^{-1}$  are obtained.

By substituting these results into the definition of the acid dissociation constant of BTB:

$$10^{-7.1} = [\text{H}^+] [\text{A}^{2-}]_{\text{BTB}} / [\text{HA}^-]_{\text{BTB}} \rightarrow [\text{H}^+] = 1.59 \times 10^{-7} \text{ mol L}^{-1}, \text{pH} = 6.8$$

From this pH, the ratio of TB that exists in the form of  $\text{A}^{2-}$  can be calculated to be 0.8%. This confirms that the absorption of the  $\text{A}^{2-}$  form of TB at 650 nm is negligible.

- (3) The pH of the solution is estimated to be 8–11 because the color of the solution is blue. Additionally, based on the significant increase of the absorbance at 500 nm originating from the  $\text{A}^{2-}$  form of PP, the pH of the solution is estimated to be 10–11. In this pH region, it is reasonable to assume that all TB, MR, and BTB exist as  $\text{A}^{2-}$ . Therefore, it is only necessary to focus on the  $\text{HA}^-/\text{A}^{2-}$  ratio of PP. Similar to the case of Q2-1, let us use the absorbance at 500 nm so that we can ignore the  $\text{HA}^-/\text{A}^{2-}$  ratio of BTB. The contributions to the absorbance of the solution at 500 nm from TB, MR, and BTB are as follows:

$$\text{TB: } \varepsilon (\text{A}^{2-}, 500 \text{ nm}) = 3500, \text{ concentration: } 3.572 \times 10^{-6} \text{ mol L}^{-1} \rightarrow \text{Absorbance: } 0.013$$

$$\text{MR: } \varepsilon (\text{A}^{2-}, 500 \text{ nm}) = 4000, \text{ concentration: } 1.547 \times 10^{-5} \text{ mol L}^{-1} \rightarrow \text{Absorbance: } 0.062$$

$$\text{BTB: } \varepsilon (500 \text{ nm}) = 3500, \text{ concentration: } 2.669 \times 10^{-5} \text{ mol L}^{-1} \rightarrow \text{Absorbance: } 0.093$$

From these results, the absorbance at 500 nm originating from PP can be calculated to be  $0.645 - 0.013 - 0.062 - 0.093 = 0.477$ .

The following equation is then obtained for the concentration of the deprotonated form of PP,  $[\text{A}^{2-}]_{\text{PP}}$ :

$$6000 [\text{A}^{2-}]_{\text{PP}} = 0.477$$

By solving the above equation, the values  $[\text{A}^{2-}]_{\text{PP}} = 7.95 \times 10^{-5} \text{ mol L}^{-1}$  and  $[\text{HA}^-]_{\text{PP}} = 1.047 \times 10^{-4} \text{ mol L}^{-1} - [\text{A}^{2-}]_{\text{PP}} = 2.52 \times 10^{-5} \text{ mol L}^{-1}$  are obtained.

By substituting these results into the definition of the acid dissociation constant of PP:

$$10^{-9.7} = [\text{H}^+] [\text{A}^{2-}] / [\text{HA}^-] \rightarrow [\text{H}^+] = 6.32 \times 10^{-11} \text{ mol L}^{-1}, \text{pH} = 10.2$$

### Problem 11. Silver electroplating

1. Because  $[Ag^+]$  and  $[Ag(OH)(CN)^-]$  are significantly lower than the concentrations of the other three species, these two will be considered later.

The three highest concentrations are:

$$[Ag(CN)_2^-] = C_{Ag,tot} \frac{\beta_2 [CN^-]^2}{\beta_2 [CN^-]^2 + \beta_3 [CN^-]^3 + \beta_4 [CN^-]^4} = C_{Ag,tot} \frac{1}{1 + \frac{\beta_3}{\beta_2} [CN^-] + \frac{\beta_4}{\beta_2} [CN^-]^2}$$

$$= C_{Ag,tot} \frac{1}{1 + 10^{1.0} + 10^{0.4}} = 0.07 \text{ mM}$$

$$[Ag(CN)_3^{2-}] = C_{Ag,tot} \frac{\beta_3 [CN^-]^3}{\beta_2 [CN^-]^2 + \beta_3 [CN^-]^3 + \beta_4 [CN^-]^4} = C_{Ag,tot} \frac{\frac{\beta_3}{\beta_2} [CN^-]}{1 + \frac{\beta_3}{\beta_2} [CN^-] + \frac{\beta_4}{\beta_2} [CN^-]^2}$$

$$= C_{Ag,tot} \frac{10^{1.0}}{1 + 10^{1.0} + 10^{0.4}} = 0.74 \text{ mM}$$

$$[Ag(CN)_4^{3-}] = C_{Ag,tot} \frac{\beta_4 [CN^-]^4}{\beta_2 [CN^-]^2 + \beta_3 [CN^-]^3 + \beta_4 [CN^-]^4} = C_{Ag,tot} \frac{\frac{\beta_4}{\beta_2} [CN^-]^2}{1 + \frac{\beta_3}{\beta_2} [CN^-] + \frac{\beta_4}{\beta_2} [CN^-]^2}$$

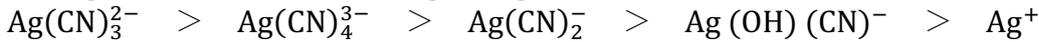
$$= C_{Ag,tot} \frac{10^{0.4}}{1 + 10^{1.0} + 10^{0.4}} = 0.19 \text{ mM}$$

The relative concentrations of  $[Ag^+]$  and  $[Ag(OH)(CN)^-]$  can be addressed with the following equation:

$$K_{OHCN} = 10^{13.20} = \frac{[Ag(OH)(CN)^-]}{[Ag^+][CN^-][OH^-]} = \frac{[Ag(OH)(CN)^-]}{[Ag^+]} \quad (\because [CN^-] = [OH^-] = 1.00 \text{ M})$$

Therefore,  $[Ag(OH)(CN)^-] \gg [Ag^+]$ .

Putting the above information together gives:



The dissolved species with the highest concentration is  $[Ag(CN)_3^{2-}] = 0.74 \text{ mM}$ .

2.  $Ag(CN)_3^{2-} + e^- \rightleftharpoons Ag(s) + 3CN^-$

$$E^\circ = 0.799 - \frac{RT}{nF} \ln \beta_3$$

$$= -0.467 \text{ [V]}$$

3. At the upper limit of  $[CN^-]$ ,  $[Ag(CN)_3^{2-}] = [Ag(CN)_4^{3-}]$

$$\beta_3 [CN^-]^3 = \beta_4 [CN^-]^4$$

$$[CN^-] = \frac{\beta_3}{\beta_4} = 10^{0.60} = 4.0 \text{ M}$$

At the lower limit,  $[Ag(CN)_2^-] = [Ag(CN)_4^{3-}]$

(note:  $[Ag(CN)_2^-] = [Ag(CN)_3^{2-}]$  is satisfied at even lower  $[CN^-]$ )

$$\beta_2 [CN^-]^2 = \beta_4 [CN^-]^4$$

$$[CN^-] = \sqrt{\frac{\beta_2}{\beta_4}} = 10^{-0.20} = 0.63 \text{ M}$$

The  $[CN^-]$  range is thus 0.63–4.0 M.

4.  $Ag^+ + e^- \rightleftharpoons Ag(s)$

$$E = E^\circ - \frac{RT}{F} \ln \frac{1}{[Ag^+]}$$

$$E = E^\circ - \frac{RT}{F} \ln \frac{\beta_3 [CN^-]^3}{[Ag(CN)_3^{2-}]}$$

$$E = 0.799 - \frac{R}{F} \frac{298.2}{1} \ln \frac{10^{21.4} \times 1.0^3}{0.74 \times 10^{-3}} = -0.652 \text{ [V]}$$

5. From  $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ , the HER equilibrium potential is:

$$E = 0 - \frac{RT}{2F} \ln \frac{1}{[\text{H}^+]^2} = -0.0592 \text{ pH}$$

$$-0.0592 \text{ pH} \leq -0.652$$

$$\text{pH} \geq 11.0$$

6. From  $p = K_{\text{H}}^{-1}[\text{HCN}(\text{aq})]$  and  $[\text{HCN}(\text{aq})] = \frac{[\text{H}^+][\text{CN}^-]}{K_{\text{a}}}$

$$p = K_{\text{H}}^{-1} \frac{[\text{H}^+][\text{CN}^-]}{K_{\text{a}}} \leq 10^{-5.0}$$

$$10^{-1.0} \frac{[\text{H}^+]10^{0.0}}{10^{-9.2}} \leq 10^{-5.0}$$

$$\text{pH} \geq 13.2$$

Problem 12. How does CO<sub>2</sub> in the atmosphere affect the pH value of seawater?

1.  $[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

[OH<sup>-</sup>] is negligible because the solution becomes acidic, and [CO<sub>3</sub><sup>2-</sup>] is also negligible because pH ≪ pK<sub>a2</sub>. Therefore,

$$[H^+] = [HCO_3^-]$$

$$[H^+] = \frac{K_{a1}[H_2CO_3]}{[H^+]}$$

$$[H^+] = \frac{K_{a1}(K_{hyd}[CO_2])}{[H^+]}$$

$$[H^+] = \frac{K_{a1}K_{hyd}(K_{gas}x_{CO_2})}{[H^+]}$$

$$[H^+] = \sqrt{K_{a1}K_{hyd}K_{gas}x_{CO_2}} = 2.5 \times 10^{-6} \text{ M}$$

$$\text{pH} = 5.60$$

$$\left( \text{pH} = \frac{pK_{a1} + pK_{hyd} + pK_{gas} - \log_{10}[x_{CO_2}]}{2} \right)$$

2. The total concentration of carbon dioxide-related species is:

$$[CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

Among these four concentrations, [CO<sub>3</sub><sup>2-</sup>] is negligible as in Q1. Moreover, [H<sub>2</sub>CO<sub>3</sub>] can also be neglected based on the relationship [H<sub>2</sub>CO<sub>3</sub>]/[CO<sub>2</sub>] = 10<sup>-2.70</sup>. Therefore, it is sufficient to consider the quantity:

$$[CO_2] + [HCO_3^-].$$

The relationship between these two concentrations is:

$$[HCO_3^-] = \frac{K_{a1}(K_{hyd}[CO_2])}{[H^+]} = 10^{-6.35 + \text{pH}}[CO_2]$$

Using this relationship, we compare the ratio of the initial and final values of [CO<sub>2</sub>] + [HCO<sub>3</sub><sup>-</sup>] for the cases where ΔpH = ±1.

(a) In the case of ΔpH = +1,

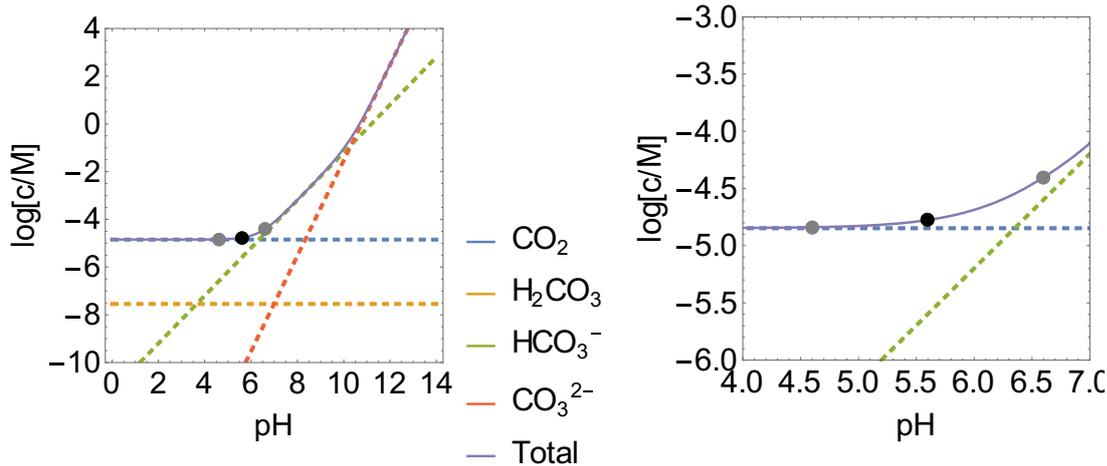
$$\frac{10^{-6.35+6.60}[CO_2] + [CO_2]}{10^{-6.35+5.60}[CO_2] + [CO_2]} = \frac{10^{+0.25} + 1}{10^{-0.75} + 1} = \frac{2.78}{1.18} = 2.4$$

Because this is more than double, the answer is (1).

(b) For ΔpH = -1,

$$\frac{10^{-1.75} + 1}{10^{-0.75} + 1} = \frac{1.02}{1.18} = 0.86$$

The answer is (3).



(The total concentration significantly increases on the higher pH side, whereas the change is small on the lower pH side.)

3. Using the relationship  $\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{\text{hyd}} + \text{p}K_{\text{gas}} - \log_{10} [x_{\text{CO}_2}]}{2}$  obtained in Q1,

$$\begin{aligned} \Delta\text{pH} &= \frac{\text{p}K_{a1} + \text{p}K_{\text{hyd}} + \text{p}K_{\text{gas}} - \log_{10}[2x_{\text{CO}_2}]}{2} - \frac{\text{p}K_{a1} + \text{p}K_{\text{hyd}} + \text{p}K_{\text{gas}} - \log_{10}[x_{\text{CO}_2}]}{2} \\ &= \frac{\log_{10}[x_{\text{CO}_2}] - \log_{10}[2x_{\text{CO}_2}]}{2} \\ &= \frac{-\log_{10} 2}{2} = -0.15 \end{aligned}$$

(This is the behavior of a weak acid.)

$$\text{pH} = 5.60 - 0.15 = 5.45$$

4.  $[\text{H}^+] + C_{\text{C-A}} = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$   
 $[\text{CO}_3^{2-}]$  is negligible as in Q1. Moreover, because the pH is  $\sim 8$ ,  $[\text{H}^+]$  and  $[\text{OH}^-]$  are negligible. Therefore,

$$\begin{aligned} C_{\text{C-A}} &= \frac{[\text{HCO}_3^-]}{[\text{H}^+]} \\ &= \frac{K_{a1}K_{\text{hyd}}K_{\text{gas}}x_{\text{CO}_2}}{[\text{H}^+]} \\ \text{pH} &= -\log_{10} \left\{ \frac{K_{a1}K_{\text{hyd}}K_{\text{gas}}x_{\text{CO}_2}}{C_{\text{C-A}}} \right\} \\ \Delta\text{pH} &= -\log_{10} \left\{ \frac{K_{a1}K_{\text{hyd}}K_{\text{gas}}(2x_{\text{CO}_2})}{C_{\text{C-A}}} \right\} + \log_{10} \left\{ \frac{K_{a1}K_{\text{hyd}}K_{\text{gas}}x_{\text{CO}_2}}{C_{\text{C-A}}} \right\} \\ &= -\log_{10} 2 = -0.30 \end{aligned}$$

(This behavior is based on the Henderson–Hasselbalch equation, and the pH change is double that in the pure water case in Q3.)

5.  $2[\text{Mg}^{2+}] + [\text{H}^+] + C_{\text{C-A}} = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$

Similar to Q4,  $[\text{CO}_3^{2-}]$ ,  $[\text{H}^+]$ , and  $[\text{OH}^-]$  are negligible.

$$\begin{aligned} 2[\text{Mg}^{2+}] + C_{\text{C-A}} &= [\text{HCO}_3^-] \\ 2C_{\text{Mg}} \frac{1}{1+K_f[\text{CO}_3^{2-}]} + C_{\text{C-A}} &= [\text{HCO}_3^-] \\ 2C_{\text{Mg}} (1 - K_f[\text{CO}_3^{2-}]) + C_{\text{C-A}} &= [\text{HCO}_3^-] \\ 2C_{\text{Mg}} + C_{\text{C-A}} &= [\text{HCO}_3^-] + 2C_{\text{Mg}}K_f[\text{CO}_3^{2-}] \\ 2C_{\text{Mg}} + C_{\text{C-A}} &= \frac{K_{a1}K_{\text{hyd}}K_{\text{gas}}x_{\text{CO}_2}}{[\text{H}^+]} + 2C_{\text{Mg}}K_f \frac{K_{a1}K_{\text{hyd}}K_{\text{gas}}x_{\text{CO}_2}}{[\text{H}^+]} \frac{K_{a2}}{[\text{H}^+]} \end{aligned}$$

By solving this quadratic equation for  $[H^+]$ , we find  $pH = 8.05$ .

In the same way, with  $x_{CO_2} \rightarrow 2x_{CO_2}$  we find  $pH = 7.80$ .

$$\Delta pH = 7.80 - 8.05 = -0.25$$

(The pH shift is milder than  $-0.30$  due to the  $MgCO_3$  equilibrium although  $\Delta pH$  is still more negative than  $-0.2$ , the threshold for coral survival).

- |               |                           |         |
|---------------|---------------------------|---------|
| 6. (Region A) | $pH = (pC_{HA} + pK_a)/2$ | $-0.15$ |
| (Region B)    | $pH = pC_{HA}$            | $-0.30$ |
| (Region C)    | $pH = pK_w/2$             | $0$     |

Region A.

7.  $-0.30$  ( $pH = pC_{HA} + pK_a - pC_{NaA}$ ).

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

1. Reaction 1:  $2 \text{CuFeS}_2 + 2 \text{SiO}_2 + 4 \text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2 \text{FeSiO}_3 + 3 \text{SO}_2$   
 Reaction 2:  $\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2 \text{Cu} + \text{SO}_2$

2. When the reaction proceeds completely, 1 mol of Cu and 2 mol of  $\text{SO}_2$  can be obtained with respect to 1 mol of  $\text{CuFeS}_2$ .

$$\text{CuFeS}_2 = 183.527 \text{ g mol}^{-1}$$

When the reaction proceeds completely from 100 kg of  $\text{CuFeS}_2$ ,

$$\text{Cu: } 100 \times 10^3 \times (63.546 / 183.527) \text{ [g]} = 3.46 \times 10^4 \text{ [g]} = 34.6 \text{ [kg]}$$

$$\text{SO}_2: 100 \times 10^3 / 183.527 \times 2 \text{ [mol]} = 1.09 \times 10^3 \text{ [mol]}$$

will be obtained.

$$\text{According to the equation } PV = nRT, V = nRT/P = 1.09 \times 10^3 \text{ [mol]} \times 8.3145 \text{ [J mol}^{-1} \text{ K}^{-1}] \times (273 + 25) \text{ [K]} / 1.00 \times 10^5 \text{ [Pa]} = 27.0 \text{ [m}^3] = 2.70 \times 10^4 \text{ [L]}$$

Answer: 34.7 kg of Cu and  $2.70 \times 10^4$  L of  $\text{SO}_2$  are obtained.

3. Based on the exothermic reaction  $2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$  and according to Le Chatelier's principle, the reaction is shifted toward the product side at low temperature and high pressure.

Answer: (2)

4.  $2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$

Let the number of moles of sulfur trioxide after the reaction be  $n(\text{SO}_3) = n$ . The number of moles of  $\text{SO}_2$  and  $\text{O}_2$  can then be calculated as  $n(\text{SO}_2) = 7 - n$  and  $n(\text{O}_2) = 3 - n/2$ . Thus, the total number of moles of gas molecules in the reaction vessel is  $n + (7 - n) + (3 - n/2) = 10 - n/2$  [mol].

According to the equation  $PV = nRT$ :

$$8.60 \times 10^5 \text{ [Pa]} \times 50.0 \times 10^{-3} \text{ [m}^3] = (10 - n/2) \text{ [mol]} \times 8.3145 \text{ [J mol}^{-1} \text{ K}^{-1}] \times 623 \text{ [K]}$$

$$n = 3.40 \text{ [mol]}$$

Answer: 3.40 mol

5. 20 kg of 32% fuming sulfuric acid consist of:

$$\text{SO}_3: 20 \times 10^3 \times 0.32 = 6.4 \times 10^3 \text{ [g]} = 6.4 \times 10^3 / 80.07 = 79.9 \text{ [mol]}$$

$$\text{H}_2\text{SO}_4: 20 \times 10^3 \times 0.68 = 13.6 \times 10^3 \text{ [g]} = 1.36 \times 10^4 / 98.08 = 138.7 \text{ [mol].}$$

1 kg of 60% sulfuric acid consists of:

$$\text{H}_2\text{SO}_4 = 600 / 98.08 = 6.12 \text{ [mol]} \text{ and } \text{H}_2\text{O} = 400 / 18.02 = 22.2 \text{ [mol].}$$

Let  $x$  [kg] equal the mass of 60% sulfuric acid required for the dilution:

$$79.9 + 138.7 + (6.12 \times x) = (20.0 + x) \times 10^3 \times 0.98 / 98.08$$

$$x = 4.84, \text{ Answer: 4.8 kg}$$

6. Let  $x$  [kg] equal the mass of water required for the dilution:

$$8.0 \times 10^3 \times 0.98 = (8.0 + x) \times 10^3 \times 0.60 \rightarrow x = 5.07. \text{ Thus, 5.07 kg of water are needed for the dilution.}$$

Now, let  $m(98)$  equal the number of moles of water required for the dilution of 1 mol of  $\text{H}_2\text{SO}_4$  to 98%:

$$\frac{98}{18 \times m(98) + 98} = 0.98$$

$$m(98) = 0.111 \text{ [mol]}$$

In this dilution process, the heat of dilution  $Q_1$  [J] is calculated as follows:

$$Q_1 = \frac{7.47 \times 10^4 \times 0.111}{0.111 + 1.80} = 4340 \text{ [J]}$$

Let  $m(60)$  equal the number of moles of water required to dilute 1 mol of  $\text{H}_2\text{SO}_4$  to 60%:

$$\frac{98}{18 \times m(60) + 98} = 0.60$$

$$m(60) = 3.63 \text{ mol}$$

In this dilution process, the heat of dilution  $Q_2$  [J] is calculated as follows:

$$Q_2 = \frac{7.47 \times 10^4 \times 3.63}{3.63 + 1.80} = 4.99 \times 10^4 \text{ [J]}$$

From the values shown above, the heat of dilution when 98% sulfuric acid containing 1 mol of  $\text{H}_2\text{SO}_4$  is diluted to 60% sulfuric acid can be calculated as:

$$Q_2 - Q_1 = 45600 \text{ [J]}$$

8.0 kg of 98% sulfuric acid contain  $8.0 \times 10^3 \times 0.98 / 98 = 80.0$  mol of  $\text{H}_2\text{SO}_4$ . Thus, the heat of dilution when 8.0 kg of 98% sulfuric acid is diluted from 98% to 60% is  $Q = 45600 \times 80.0 = 3.65 \times 10^6$  [J].

Answer:  $3.7 \times 10^6$  J

The produced heat  $Q$  [J] can raise the temperature of 10 kg of water ( $0^\circ\text{C}$ ) by:

$$3.65 \times 10^6 / (10.0 \times 10^3 \times 4.18) = 87.3$$

Answer :  $87^\circ\text{C}$

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

1-1. (1)  $\Delta H = (335 + 467 - 392 - 426) \text{ [kJ mol}^{-1}] = -16 \text{ [kJ mol}^{-1}]$

(2)  $\Delta H = (451 + 467 - 500 - 426) \text{ [kJ mol}^{-1}] = -8 \text{ [kJ mol}^{-1}]$

1-2. Let  $\text{BE}(\text{Si-Cl}^{\text{a}}) = x \text{ [kJ mol}^{-1}]$  and  $\text{BE}(\text{Si-Cl}^{\text{e}}) = y \text{ [kJ mol}^{-1}]$

From Eq.(2-1):  $451 \times 4 - (400 + x + 3 y) = 14$ ; from Eq.(3):  $451 \times 4 - (2 x + 3 y) = 50$   
 $x + 3 y = 1390$ ,  $2 x + 3 y = 1754 \rightarrow x = 364$ ,  $y = 342$

Answer:  $\text{BE}(\text{Si-Cl}^{\text{a}}) = 364 \text{ [kJ mol}^{-1}]$ ,  $\text{BE}(\text{Si-Cl}^{\text{e}}) = 342 \text{ [kJ mol}^{-1}]$

1-3. (1) A one-step reaction with a larger reaction barrier relative to the silicon case: (ii)

(2) A two-step reaction with a small barrier for the first step: (iii)

2-1. According to the definition equation:  $(\chi_{\text{A}} - \chi_{\text{B}})^2 = D_{\text{AB}} - (D_{\text{AA}} + D_{\text{BB}}) / 2$

$(\chi_{\text{N}} - \chi_{\text{H}})^2 = D_{\text{NH}} - (D_{\text{NN}} + D_{\text{HH}}) / 2$

Thus,  $D_{\text{NH}} = (\chi_{\text{N}} - \chi_{\text{H}})^2 + (D_{\text{NN}} + D_{\text{HH}}) / 2 = (3.04 - 2.10)^2 + ((158 / 96.5) + (436 / 96.5)) / 2$   
 $= 0.8836 + 3.0777 = 3.961 \text{ [eV]} = 382 \text{ [kJ mol}^{-1}]$

Similarly,  $(\chi_{\text{Cl}} - \chi_{\text{H}})^2 = D_{\text{ClH}} - (D_{\text{ClCl}} + D_{\text{HH}}) / 2$

Thus,  $D_{\text{ClCl}} = 2 \times (D_{\text{ClH}} - (\chi_{\text{Cl}} - \chi_{\text{H}})^2) - D_{\text{HH}} = 2 \times ((426 / 96.5) - (3.16 - 2.1)^2) - (436 / 96.5)$   
 $= 2 \times 3.291 - 4.518 = 2.064 \text{ [eV]} = 199 \text{ [kJ mol}^{-1}]$

Furthermore,  $(\chi_{\text{Cl}} - \chi_{\text{N}})^2 = D_{\text{NCl}} - (D_{\text{ClCl}} + D_{\text{NN}}) / 2$

Thus,  $D_{\text{NCl}} = (\chi_{\text{Cl}} - \chi_{\text{N}})^2 + (D_{\text{ClCl}} + D_{\text{NN}}) / 2 = (3.16 - 3.04)^2 + (199 / 96.5 + 158 / 96.5) / 2 = 1.864$   
 $\text{[eV]} = 179.9 \text{ [kJ mol}^{-1}]$

Answer:  $D_{\text{NH}} = 382 \text{ [kJ mol}^{-1}]$ ,  $D_{\text{ClCl}} = 199 \text{ [kJ mol}^{-1}]$ ,  $D_{\text{NCl}} = 180 \text{ [kJ mol}^{-1}]$ .

2-2. Answer: A:  $\text{H}_2\text{NOH}$ ; B:  $\text{HCl}$ ; C:  $\text{NH}_3$ ; D:  $\text{HOCl}$

Broken bonds: N-Cl (180 [kJ mol<sup>-1</sup>]), O-H (467 [kJ mol<sup>-1</sup>])

Formed bonds: N-H (382 [kJ mol<sup>-1</sup>]), Cl-O (206 [kJ mol<sup>-1</sup>])

Accordingly,  $\Delta H = (180 + 467) - (382 + 206) = 59 \text{ [kJ mol}^{-1}]$

Answer:  $Q = 59 \text{ [kJ]}$

2-3. Considering the electron distributions of nitrogen and chlorine below, their  $Z^{\text{VE}}_{\text{eff}}$  values can be estimated as follows:

N:  $(1s)^2(2s)^2(2p)^3$ ,  $Z^{\text{VE}}_{\text{eff}}(\text{N}) = 7 - (0.35 \times 4) - (0.85 \times 2) = 3.9$

Cl:  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^5$ ,  $Z^{\text{VE}}_{\text{eff}}(\text{Cl}) = 6.1$

Accordingly, their Allred-Rochow electronegativities are:

$\chi_{\text{AR}}(\text{N}) = 3590 \times ((3.9 - 0.35) / 70^2) + 0.744 = 3.34$

$\chi_{\text{AR}}(\text{Cl}) = 3590 \times ((6.1 - 0.35) / 99^2) + 0.744 = 2.85$

Thus, the polarity of the N-Cl bond should be considered to be  $\text{N}^{\ominus}\text{-Cl}^{\oplus}$ , based on the Allred-Rochow electronegativities.

### Problem 15. Sulfur in hot springs and volcanoes

1. Molecular weight of CdS = 144.482

CdS 9.50 [mg] =  $(9.50 / 144.482) = 6.58 \times 10^{-5}$  [mol]  $\rightarrow$  number of moles of H<sub>2</sub>S

According to the reaction equation:  $I_2 + 2 S_2O_3^{2-} \rightarrow 2 I^- + S_4O_6^{2-}$ , the number of moles of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is:

$$2.50 \times 10^{-2} \times (7.30 \times 10^{-3}) \times 2 = 3.65 \times 10^{-4} \text{ [mol]}$$

The mass of sulfur is:  $(6.58 \times 10^{-5} + 3.65 \times 10^{-4} \times 2) \times 32.068 = 255.2 \times 10^{-4}$  [g] = 25.5 [mg]

Accordingly, the mass of sulfur in 1 kg of hot spring water is 255 [mg kg<sup>-1</sup>]

Answer: 255 mg kg<sup>-1</sup>

2.  $H_2S \rightleftharpoons H^+ + HS^-$ :  $K_1 = 9.50 \times 10^{-8}$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]}$$

$HS^- \rightleftharpoons H^+ + S^{2-}$ :  $K_2 = 1.30 \times 10^{-14}$

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]}$$

pH = 8.00 corresponds to  $[H^+] = 1.00 \times 10^{-8}$  [mol L<sup>-1</sup>]

Accordingly,

$$[HS^-] = \frac{[H^+][S^{2-}]}{K_2} = \frac{1.00 \times 10^{-8} \times 1.00 \times 10^{-8}}{1.3 \times 10^{-14}} = 7.692 \times 10^{-3} \text{ [mol L}^{-1}\text{]}, \text{ and}$$

$$[H_2S] = \frac{[H^+][HS^-]}{K_1} = \frac{[H^+]^2[S^{2-}]}{K_1 K_2} = \frac{(1.00 \times 10^{-8})^2 \times 1.00 \times 10^{-8}}{9.5 \times 10^{-8} \times 1.3 \times 10^{-14}} = 8.097 \times 10^{-4} \text{ [mol L}^{-1}\text{]}$$

Thus,  $[S^{2-}] + [HS^-] + [H_2S] = 1.00 \times 10^{-8} + 7.692 \times 10^{-3} + 8.097 \times 10^{-4} = 8.502 \times 10^{-3}$  [mol L<sup>-1</sup>]

The amount of S atoms derived from S<sup>2-</sup>, HS<sup>-</sup>, and H<sub>2</sub>S is:

$$8.502 \times 10^{-3} \times 32.068 = 2.7274 \times 10^{-1} \text{ [g]} = 272.74 \text{ [mg]}.$$

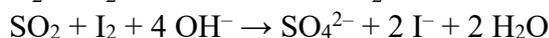
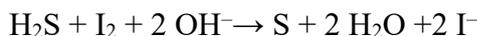
The hot spring water contains 5.90 mg of S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, and the mass of the S atoms from S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is:

$$5.90 \times (64.136 / 112.1342) = 3.375 \text{ [mg]}$$

Finally, the total amount of sulfur is  $272.74 + 3.375 = 276.12$  [mg]

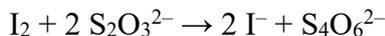
Answer: 276 mg kg<sup>-1</sup>

3. When the volcanic gas is absorbed by the aqueous solution of I<sub>2</sub>/KI, both the following reactions occur:



Thus, both H<sub>2</sub>S and SO<sub>2</sub> should react with I<sub>2</sub> in a 1:1 ratio.

In the titration test in beaker **B**, the residual I<sub>2</sub> should react with sodium thiosulfate as follows:



The number of moles of sodium thiosulfate consumed is  $2.00 \times 10^{-2} \times (73.0 \times 10^{-3}) = 1.46 \times 10^{-3}$  [mol]. Accordingly, the residual amount of I<sub>2</sub> in beaker **B** is  $1.46 \times 10^{-3} / 2 = 7.30 \times 10^{-4}$  [mol].

Based on these calculated values, the amount of residual I<sub>2</sub> in the initial absorption solution (1.00 L) is  $7.30 \times 10^{-3}$  [mol].

Because the absorption solution contains  $2.00 \times 10^{-2}$  [mol L<sup>-1</sup>]  $\times$  500 [mL] =  $1.00 \times 10^{-2}$  [mol] of I<sub>2</sub> before the absorption,  $1.00 \times 10^{-2}$  [mol]  $-$   $7.30 \times 10^{-3}$  [mol] =  $2.70 \times 10^{-3}$  [mol] of I<sub>2</sub> was consumed through the gas absorption.

Additionally, 41.5 mg of BaSO<sub>4</sub> (molecular weight: 233.3926), i.e.,  $(41.5 \times 10^{-3}) / 233 = 1.778 \times 10^{-4}$  [mol] of BaSO<sub>4</sub>, was obtained from the reaction in beaker **A**, meaning that  $1.778 \times 10^{-4} \times 10 = 1.778 \times 10^{-3}$  mol of SO<sub>2</sub> reacted in the absorption solution. Accordingly, when the volcano gas was absorbed into the solution,  $1.778 \times 10^{-3}$  mol of I<sub>2</sub> was consumed in the absorption solution.

Thus, the amount of  $I_2$  consumed by the reaction with  $H_2S$  is  $2.70 \times 10^{-3} - 1.778 \times 10^{-3} = 9.22 \times 10^{-4}$  mol, which is the same as the amount of  $H_2S$  absorbed from the volcanic gas.

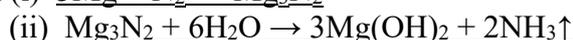
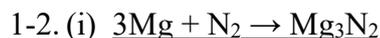
Considering the combined results, the concentrations of  $H_2S$  and  $SO_2$  in the volcanic gas can be calculated as  $9.22 \times 10^{-5}$  [mol L<sup>-1</sup>] and  $1.78 \times 10^{-4}$  [mol L<sup>-1</sup>], respectively.

Answer:  $[H_2S] = 9.22 \times 10^{-5}$  [mol L<sup>-1</sup>],  $[SO_2] = 1.78 \times 10^{-4}$  [mol L<sup>-1</sup>].

Problem 16. Identification of unknown compounds and allotropes

1-1.

A	$\text{MgH}_2$
B	$\text{Mg(OH)}_2$
C	$\text{MgO}$
D	$\text{NH}_3$



1-3. 2 mol of  $\text{NH}_3$  gas is generated from 3 mol of Mg.

$$M = M_w(\text{Mg}) \cdot n(\text{Mg}) = 24.305 \times \frac{PV}{RT} \times \frac{3}{2} = 0.18 \text{ [g]}$$

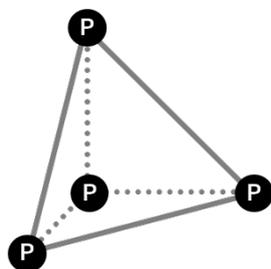
2-1.

E	<u>1</u>
F	<u>2</u>

2-2. One cubic unit cell contains 4 molecules of  $\text{C}_{60}$ , which corresponds to a total of 240 C atoms.

Their weight is  $\frac{M_w(\text{C}) \times 240}{N_A}$  [g]. The volume of one cubic unit cell is  $(1.41 \times 10^{-7})^3$  [ $\text{cm}^3$ ]. The density is therefore 1.71 [g  $\text{cm}^{-3}$ ].

2-3.



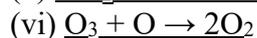
(Tetrahedral structure)



2-5.  $N$  [mol] of  $\text{I}_2$  is generated from  $N$  [mol] of ozone according to the equation in Q2-4.



The required amount of  $\text{Na}_2\text{S}_2\text{O}_3 = 0.20 \times 0.0035$  [mol], therefore the amount of  $\text{I}_2$  is  $3.5 \times 10^{-4}$  [mol].



Problem 17. Metal Oxides

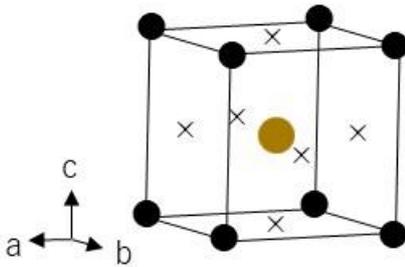
1-1.  $\{1 - (4/3\pi r^3 \times 4) / (4r / 2^{1/2})^3\} \times 100 = 26\%$

1-2. Octahedral void:  $(8^{1/2}r - 2r) / 2 = 0.05799\dots$  0.0580 nm

Tetrahedral void:  $(6^{1/2}r - 2r) / 2 = 0.03146\dots$  0.0315 nm

1-3. The number of octahedral and tetrahedral voids formed by  $n$  oxide ions is  $n$  and  $2n$ , respectively. Therefore, the chemical formula is  $AB_2O_4$  ( $x = 1, y = 2, z = 4$ ).

1-4.



2-1.  $\Delta H_{Lexp} = (635 + 193 + 498 \times 0.5 + 590 + 1010 + 878 - 141) = 3414 \text{ kJ mol}^{-1}$

2-2.

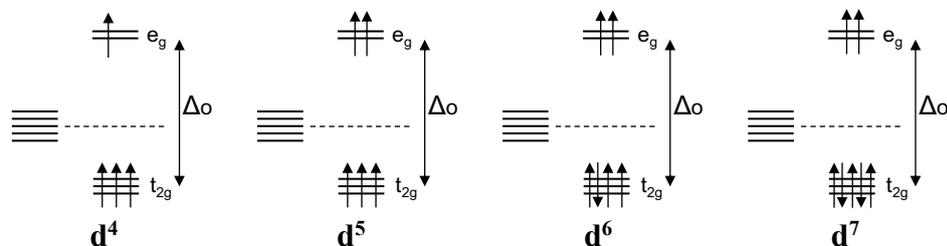
$$E_1 = -\frac{6e^2}{\pi\epsilon_0 d} \quad E_2 = +\frac{6\sqrt{2}e^2}{\pi\epsilon_0 d}$$

2-3.  $\Delta H_{Lcalc} = 3.47 \times 10^3 \text{ kJ mol}^{-1}$  (answer with three significant digits).

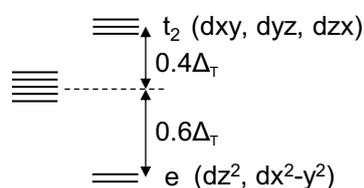
Note that the difference in  $\Delta H_{Lexp}$  and  $\Delta H_{Lcalc}$  is small (less than 1.5%).

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

- The  $e_g$  orbitals are:  $d_{z^2}$  and  $d_{x^2-y^2}$ ; the  $t_{2g}$  orbitals are:  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$
- The  $e_g$  orbitals:  $+0.6\Delta_o$ ; the  $t_{2g}$  orbitals:  $-0.4\Delta_o$
- CFSE  $d^4$ :  $-0.6\Delta_o$ ;  $d^5$ : 0;  $d^6$ :  $-0.4\Delta_o$ ;  $d^7$ :  $-0.8\Delta_o$



4.



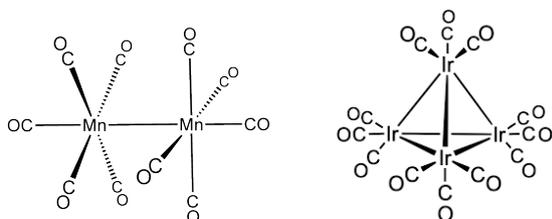
5.

$$E = h \frac{c}{\lambda} \times N_A = (6.626 \times 10^{-34}) \times (2.998 \times 10^8) \div (500 \times 10^{-9}) \times (6.022 \times 10^{23}) \times 10^{-3}$$

$$= 2.392 \times 10^2 = 2.39 \times 10^2$$

$$2.39 \times 10^2 [\text{kJ mol}^{-1}]$$

6.



Mn (group 7) supplies 7 electrons, the five CO ligands supply 10 electrons, and 1 electron is supplied by the neighboring Mn atom, thus satisfying the 18-electron rule. Ir (group 9) supplies 9 electrons, the three CO ligands supply 6 electrons, and 3 electrons are supplied by the neighboring Ir atoms, thus satisfying the 18-electron rule.

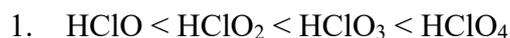
7-1.  $[\{(0.55 \text{ mL} / (R \times 273 \times 10^6 / 10^5) \text{ mL mol}^{-1}) \times 195 \text{ g mol}^{-1}\} / 0.010 \text{ g} \times 1.0] \times 100 = 47.3 \% = 47\%$

7-2. Number of CO molecules (A):  $(0.55 \text{ mL} / (R \times 273 \times 10^6 / 10^5) \text{ mL mol}^{-1}) \times (6.02 \times 10^{23} \text{ mol}^{-1}) = 1.463 \times 10^{19} / \text{g-cat}$   
 Number of CO molecules per 1.0 g of Pt (B):  $A / \{(0.01 \times 1)\} = 1.463 \times 10^{21} / \text{g-Pt}$

7-3. Surface area per 1 g of Pt (C)  $[\text{m}^2 \text{ g}^{-1}] = B \times (8.0 \times 10^{-2} \text{ nm}^2) \times 10^{-18} = 117.0 \dots \text{ m}^2 \text{ g}^{-1} = 117 \text{ m}^2 \text{ g}^{-1}$

7-4.  $\alpha$ : number of Pt metal particles;  $r$ : radius of a Pt metal particle [m];  $\rho$ : density of Pt metal [ $\text{g cm}^{-3}$ ]  
Surface area of 1.0 g of Pt metal (D):  $\{4\pi r^2 \times \alpha\} / 0.01 = C$   
Volume of 1.0 g of Pt metal (E):  $\{(4/3)\pi r^3 \times \alpha\} / 0.01 = 1 / (\rho \times 10^6)$   
 $\alpha$  can be eliminated by taking (E)/(D) to obtain the following equation:  $r / 3 = 1 / (C \times \rho \times 10^6)$   
Since  $d$  [nm] is  $2 r \times 10^9$ ,  $d = 6000 / (C \times \rho) = 2.39 \text{ nm} = 2.4 \text{ nm}$

### Problem 19. Acids and bases

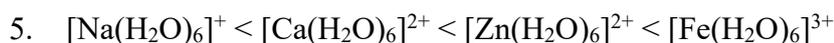


The more stable the conjugate base, the stronger the acid is. The stability of the conjugate base increase with the number of resonance structures. The number of resonance structures of the conjugate base of oxoacids of chlorine increases in the order of  $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$ .

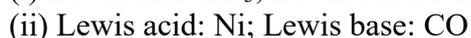
2.  $567 + 1312 - 328 = 1551 \text{ kJ mol}^{-1}$

3.  $298 + 1312 - 295 = 1315 \text{ kJ mol}^{-1}$

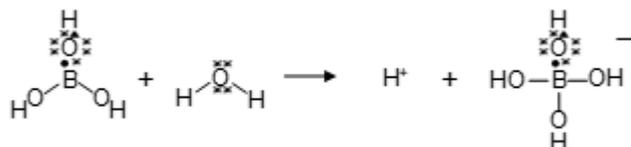
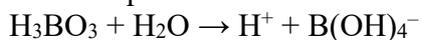
4.  $|\Delta H_{\text{HF}}| > |\Delta H_{\text{HI}}|$ ,  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$



The strength of aqua acids typically increases with increasing positive charge of the central metal ion and with decreasing ionic radius. The ionic radius decreases moving from left to right in any given period.

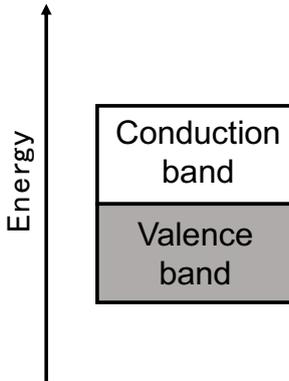


7. The boron atom in  $\text{H}_3\text{BO}_3$  is electron deficient; thus,  $\text{H}_3\text{BO}_3$  is a Lewis acid and reacts with water via the equation:



Problem 20. Semiconductors

1.



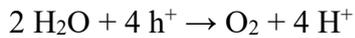
2. As the electron configuration of Si is  $[\text{Ne}]3s^23p^2$ , the hole-doping of Si requires elements with a smaller number of valence electrons than Si. Therefore, doping Si with B, which has the electron configuration  $[\text{He}]2s^22p^1$ , or Ga, which has the configuration  $[\text{Ar}]3d^{10}4s^24p^1$ , would result in the appearance of p-type properties.

3-1. The following reaction proceeds under an  $\text{H}_2$  flow, resulting in the loss of oxide ions from  $\text{TiO}_2$ :  
 $\text{TiO}_2 + x \text{H}_2 \rightarrow \text{TiO}_{2-x} + x \text{H}_2\text{O}$   
Accordingly,  $\text{TiO}_2$  is doped with electrons and the resulting  $\text{TiO}_{2-x}$  exhibits n-type semiconductor properties.

3-2.

$$1.23 \text{ V from } \Delta G = -2FE$$

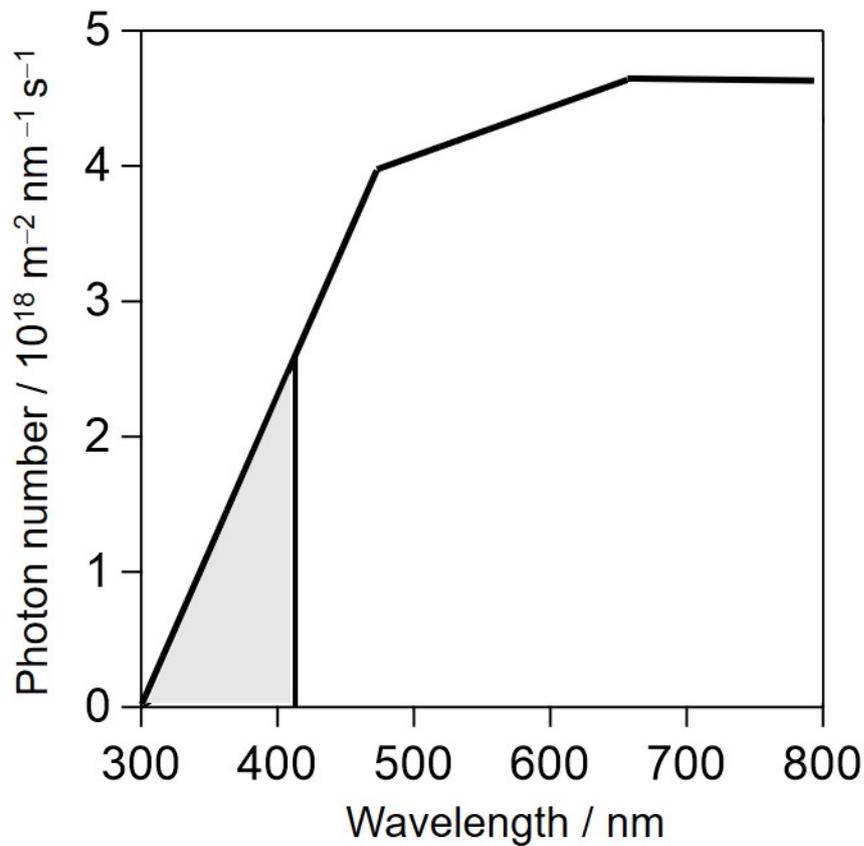
3-3.



3-4. From  $E = hc/\lambda$

$$\lambda = 1240/3 = 413 \text{ nm}$$

The conversion efficiency is ca. 6.5% when the sunlight spectrum is approximated as shown in the figure below.  $\Rightarrow$  (b)



3-5.  $E = hc/\lambda = 1240/350 = 3.543 \text{ eV} = 5.675 \times 10^{-19} \text{ J}$

Photon number = (light intensity) / (energy per photon)

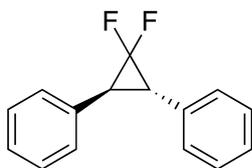
$$= 1 \text{ [J s}^{-1}] / (5.675 \times 10^{-19})$$

$$= 1.762 \times 10^{18}$$

$$\{(0.05 \times 10^{-6} \text{ [mol s}^{-1}] \times 2 \times 6.02 \times 10^{23}) / (1.762 \times 10^{18})\} \times 100 = 3.42\%$$

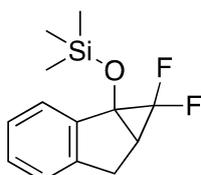
Problem 21. Carbenes and non-benzenoid aromatic compounds

1.



Similar to the Ruppert-Prakash reagent ( $\text{Me}_3\text{SiCF}_3$ ),  $\text{Me}_3\text{Si-CF}_2\text{Br}$  is converted into a difluorocarbene in the presence of bromide, which attacks the silicon atom. The NMR spectra indicate a symmetric structure for **A**.

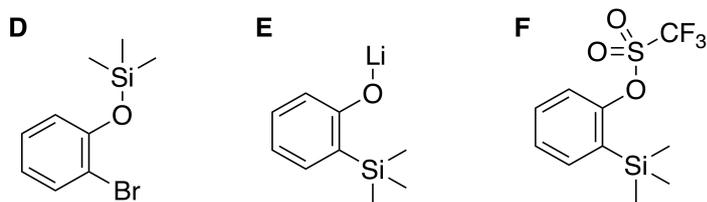
2.



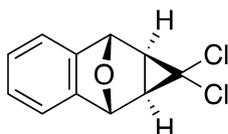
$\text{Me}_3\text{SiBr}$  (TMSBr) is generated together with the fluorocarbene. TMSBr then transforms the ketone into a silylenol ether, before a subsequent cyclopropanation affords **B**.

3. The ring-opening of the cyclopropane followed by rearomatization furnishes **C**.

4.



5.



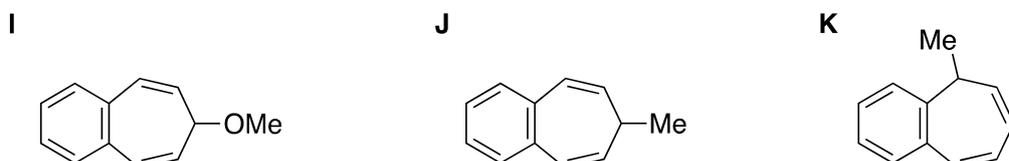
**G** is obtained after the addition of a dichlorocarbene to the double bond and the formation of the cyclopropane moiety. Albeit that the stereochemistry is important for the ring-opening, it is not requested here.

6.

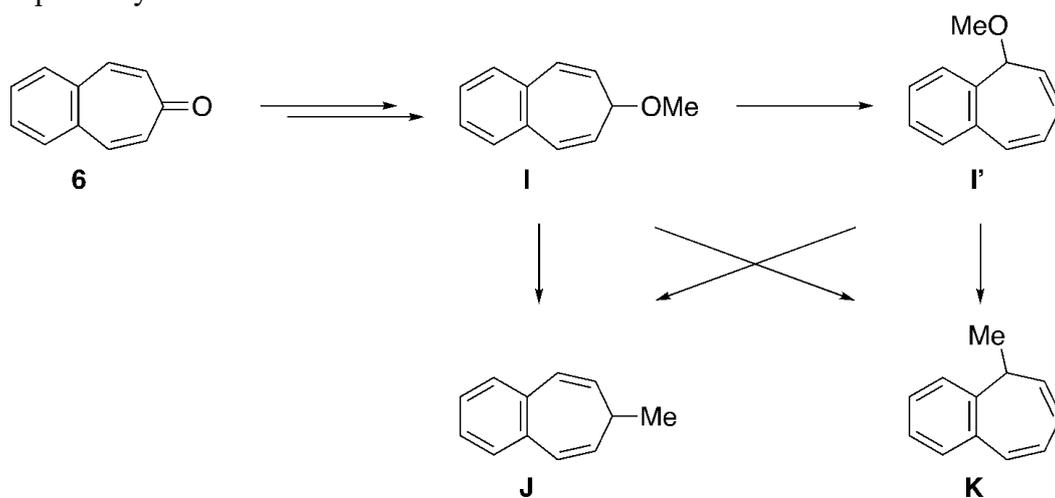


Based on the molecular formula, only one reduction has occurred.

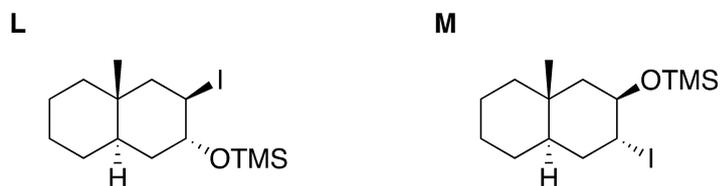
7.



The whole transformation is shown below, whereby the formation of the intermediary cycloheptatrienyl cation is crucial.



8.

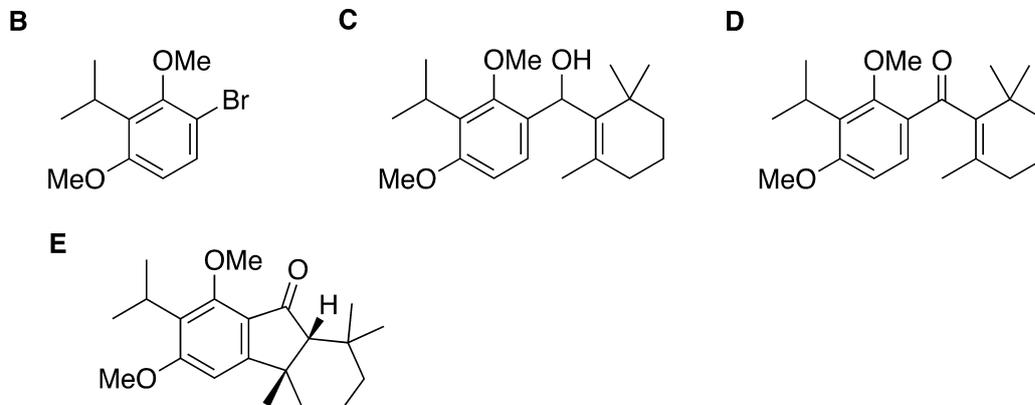


Diasterial ring opening dominates in six-membered ring systems.

## Problem 22. Nazarov cyclization

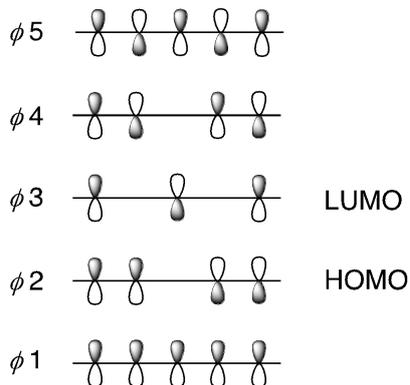
1. a, d  
Bicyclic structures that contain rigid five-membered rings rarely engage in a *trans* fusion.

2.



Compound **2** is brominated either at the *para*-position or at the *ortho*-position to give **B**. **C** is generated via a halogen-lithium exchange and a subsequent addition to the aldehyde. **D** is obtained from an oxidation of the OH group. **E** is formed via a Nazarov cyclization, followed by deprotonation and aromatization.

### Optional problem

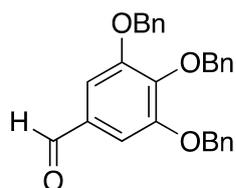


Problem 23. Tea party

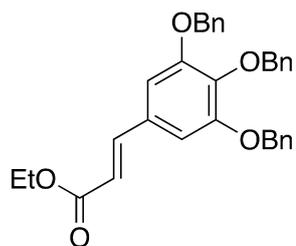
1. 2*R*, 3*R*
2. HCl, MeOH
3. PhCH<sub>2</sub>Cl, NaH

4.

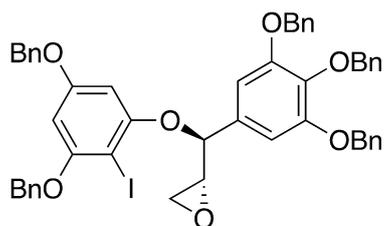
**C**



**D**

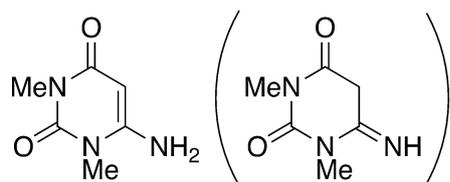


**E**

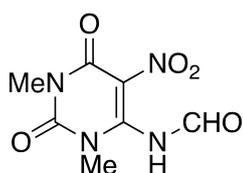


5.

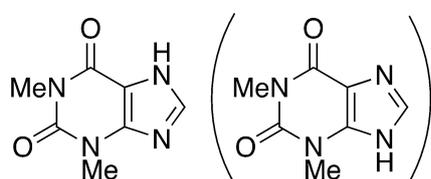
**F**



**G**



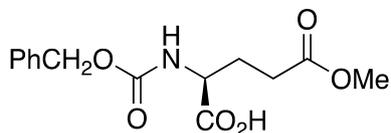
**H**



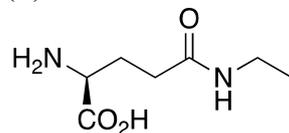
6. 1) NaH, 2) MeI

7.

**J**

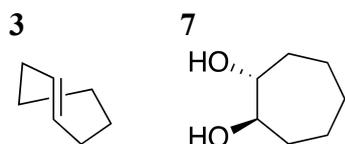


(+)-theanine

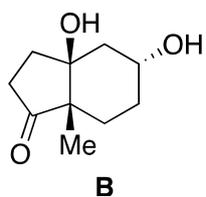


Problem 24. E-Z chemistry

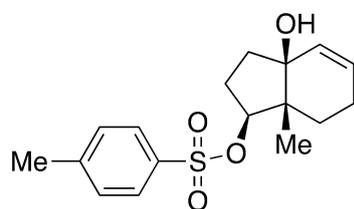
1.



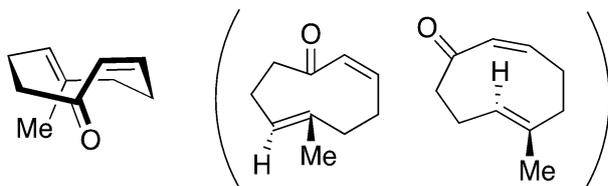
2.



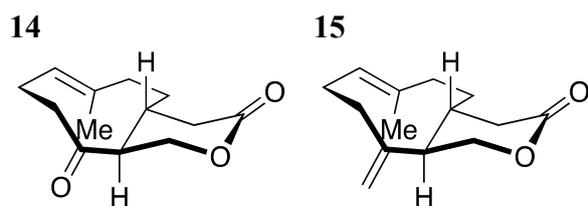
3.



4.

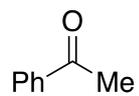


5.

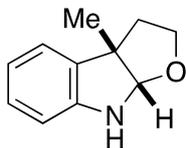


## Problem 25. Fischer indole synthesis

1.

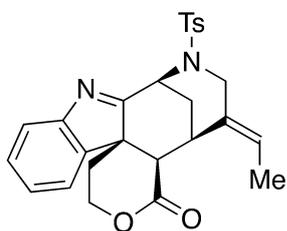


2.

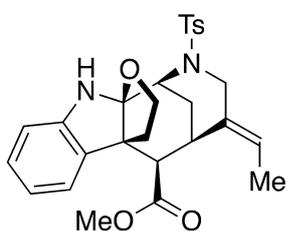


3.

**14**

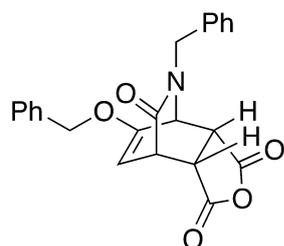


**15**

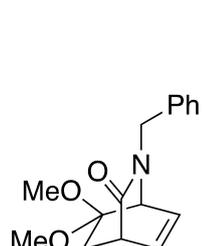


4.

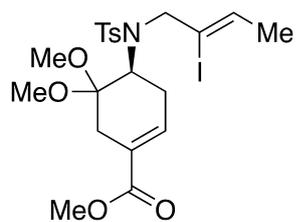
**17**



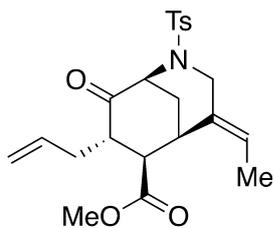
**18**



5.



6.

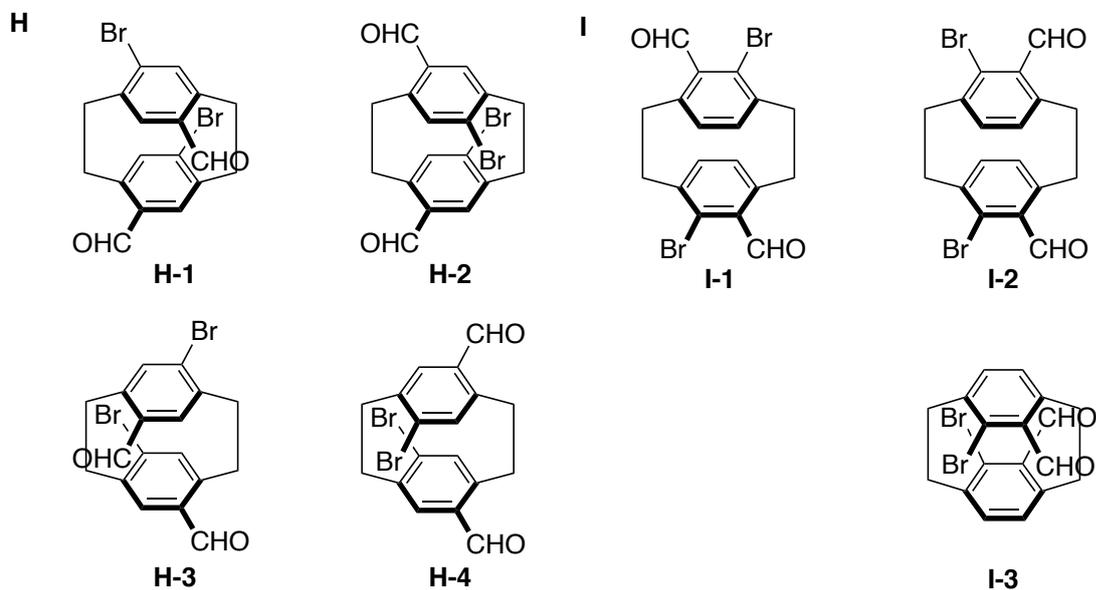


Problem 26. Planar chirality

1. **B, D, E**

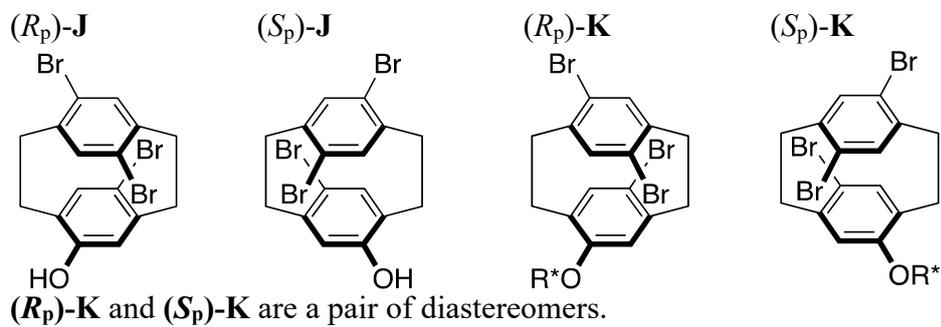
Only **C** is a *meso*-compound.

2.



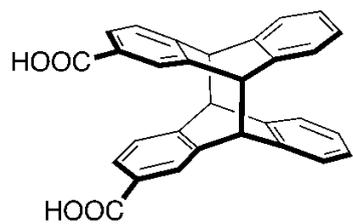
**I-1** is a *meso*-compound. (**H-1, H-3**), (**H-2, H-4**), and (**I-2, I-3**) are pairs of enantiomers.

3.

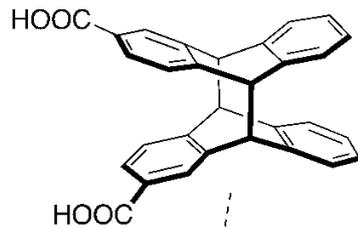


4.

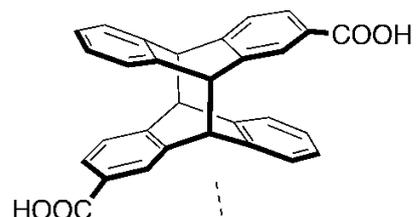
**M-1**



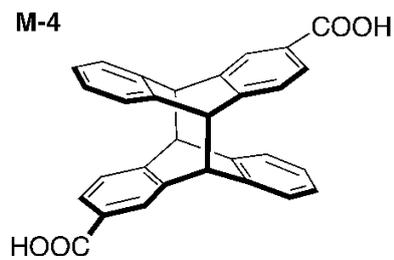
**M-2**



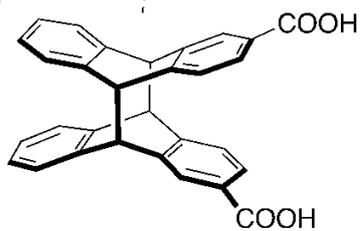
**M-3**



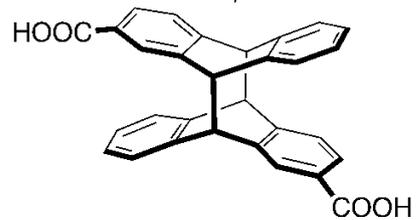
**M-4**



**M-5**



**M-6**



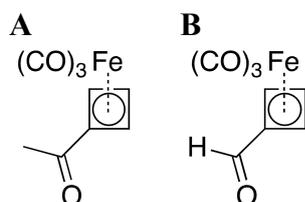
enantiomer

enantiomer

**M-1** and **M-4** are *meso*-compounds.

## Problem 27. Cyclobutadiene

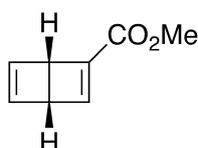
1.



**A**; Friedel-Crafts acylation. **B**; Vilsmeier formylation.

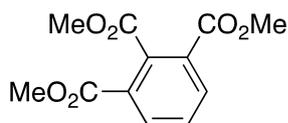
Both reactions furnish more electron-deficient products so that the subsequent second substitution is much slower than the first.

2.



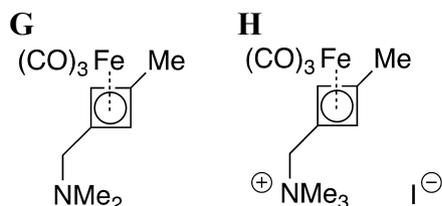
The reaction is a [2+2]-cycloaddition-like reaction to give a [2.2.0]-bicycle. The stereochemistry is not known exactly, as the reaction mechanism has not yet been elucidated unequivocally. So the stereochemistry is not required. In fact, the cis isomer is produced exclusively on account of the bicyclic ring strain.

3-1.

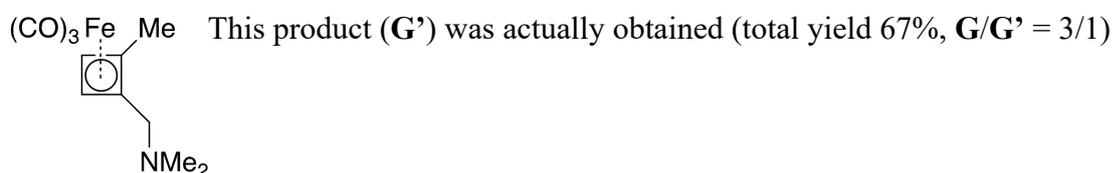


The target compound is obtained from a [4+2] cycloaddition reaction followed by decarboxylative aromatization.

3-2.

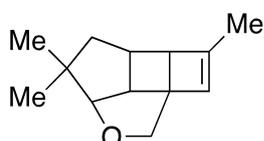


Compound **G** is formed via an electrophilic substitution reaction, wherein  $\text{Me}_2\text{N-H}$  works as a leaving group.

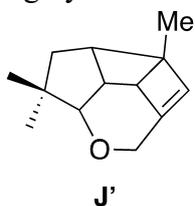


Compound **H** is an ammonium salt generated *in situ* that undergoes a substitution reaction with an alkoxide.

3-3.

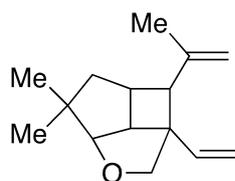


After demetallation by cerium ammonium nitrate, a [2+2]-cycloaddition-like reaction occurs to give product **J**. The steric effect of the methyl group and the ring strain can be expected to direct the reaction toward **J**. Another isomer (**J'**) might be considered, albeit that its structure would be highly strained given the presence of a double bond at the bridgehead position.

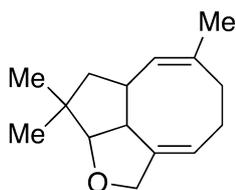


3-4.

**K**



**L**



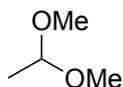
The ring-opening metathesis of **J** with ethylene gives **K**, which undergoes the Cope rearrangement to give **L**.

## Problem 28. Onion-like complexes

- $0.120 \text{ nm} \times 6 + 0.143 \text{ nm} \times 12 + 0.140 \text{ nm} \times 12 = 4.116 \text{ nm} \sim 4.12 \text{ nm}$   
 $4.12 \text{ nm} / \pi = 1.31 \text{ nm}$  (reported value: 1.32 nm)
- $0.120 \text{ nm} \times 9 + 0.143 \text{ nm} \times 18 + 0.140 \text{ nm} \times 18 = 6.174 \text{ nm} \sim 6.17 \text{ nm}$   
 $6.17 \text{ nm} / \pi = 1.96 \text{ nm}$  (reported value: 1.98 nm)
- $(1.96 \text{ nm} - 1.31 \text{ nm}) / 2 = 0.325 \text{ nm} \sim 0.33 \text{ nm}$
- The half width of benzene (0.37 nm) is longer than the width of the interspace of the two rings (0.33 nm; *cf.* Q3). Therefore, the benzene ring cannot tilt, which means only configuration C is viable. This conclusion is also applicable to the interspace between benzene and alkyne moieties.
- $1.31 \text{ nm} - 0.65 \text{ nm} = 0.66 \text{ nm}$  (reported value: 0.71 nm)
- $\Delta G = -RT \ln K$   
 $K = 8.14 \times 10^2$   
 $K = (1-a)/ca^2$   
where  $a$  is the ratio of free [6]CPP (= free [11]CPP) and  $c$  the total concentration of [6]CPP.  
In this case,  $c = 0.400 \text{ mmol L}^{-1}$  as two solutions are mixed in the same volume ratio.  
This affords  $a = 0.794$  and consequently  
[free [6]CPP] =  $ca = 3.18 \times 10^{-4} \text{ mol L}^{-1}$
- (a) and (d) are correct.  
b: The [n]CPPs ( $n = 9-12$ ) do not quantitatively form complexes because their peaks remain unchanged after the addition of the second equivalent of [13]CPP.  
c: As the complex precipitates from the solution, its peak must vanish.  
e: The peak attributed to [8]CPP disappears after the addition of the first equivalent of [13]CPP. The new peak should thus be ascribed exclusively to [13]CPP.

### Problem 29. Hydrogen-bonded capsules

1.



2. (b)

3. (c)

The graph shows that two equivalents of DBU (0.5 mmol) lead to the complete dimerization of **D**. Accordingly, every molecule contains two deprotonated sites and each dimeric capsule of **D** should contain four deprotonated sites.

In the original report, this graph was obtained in the presence of pyrazine; this divergence can be ignored here.

4.

$$\frac{1300}{77} = \frac{[\text{pyrazine@host}][\text{free dioxane}]}{[\text{dioxane@host}][\text{free pyrazine}]} = \frac{75 [\text{pyrazine@host}]}{25 [\text{free pyrazine}]} = \frac{75 [a]}{25 [1 - a]}$$

$$a = 0.85$$

Thus, 85% of pyrazine is encapsulated by **D**.

5. (a): (1)

The OH groups are acetylated, which leads to the retro-dimerization of the capsule and hence the release of benzene.

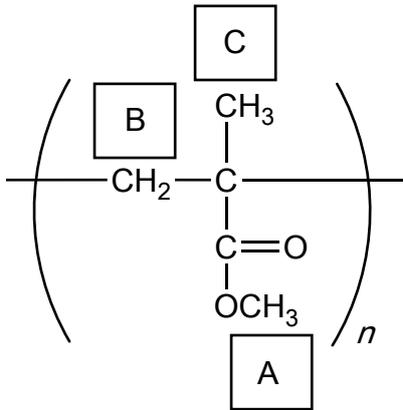
(b): (3)

Upon dilution with chloroform, chloroform is gradually encapsulated under concomitant release of benzene.

6. The reaction **B**→**C** affords a methylene-bridged capsule. Due to this covalent bridging, reversible association and dissociation is not possible anymore, and the guest molecule can no longer be released.

Problem 30. Synthesis and structural analysis of polymers

1.



2. (b)

3. (1) g A  
 (2) d B  
 (3) a D

4. C

5.  $d[M_1]/d[M_2] = [M_1]/[M_2] \times (r_1[M_1] + [M_2]) / ([M_1] + r_2[M_2])$

As the content of  $M_1$  in the polymer is 50 mol%,  $d[M_1]/d[M_2] = 1.0$ ,  $r_1 = 0.40$ , and  $r_2 = 0.10$  can be substituted into the above equation:

$$1.0 = [M_1]/[M_2] \times (0.40[M_1] + [M_2]) / ([M_1] + 0.10[M_2])$$

$$[M_2] \times ([M_1] + 0.10[M_2]) = [M_1] \times (0.40[M_1] + [M_2])$$

$$0.10[M_2]^2 = 0.40[M_1]^2$$

$$([M_1]/[M_2])^2 = 0.10/0.40 = 0.25$$

$$[M_1]/[M_2] = 0.50$$

Therefore, the content of  $M_1$  in the total monomer mixture ( $[M_1]/([M_1] + [M_2])$ ) is 1/3.  
 33 mol%

6. Polymer obtained:

1 B

2 D

Site where the initiator reacts:

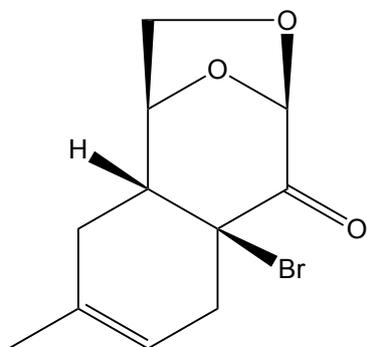
1 F

2 G

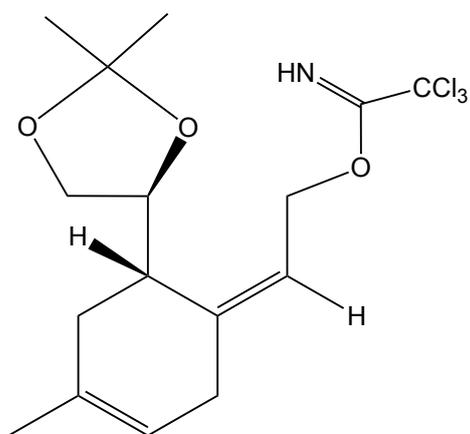
Problem 31. Total synthesis of tetrodotoxin

1.

2

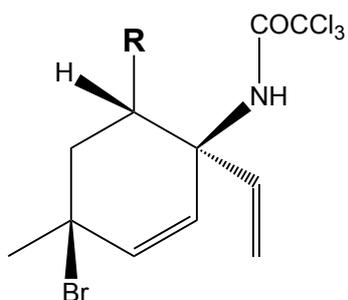


6

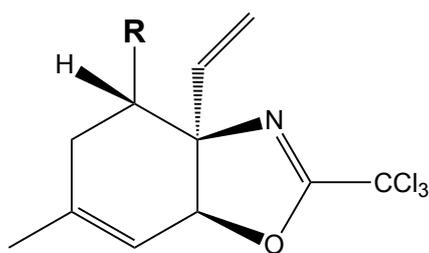


2.

9

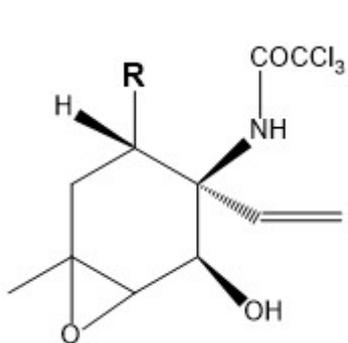


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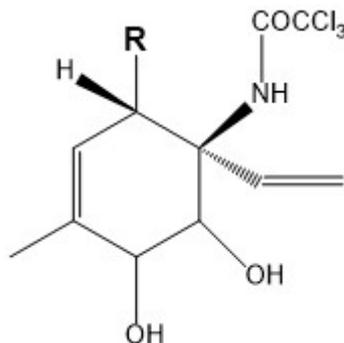


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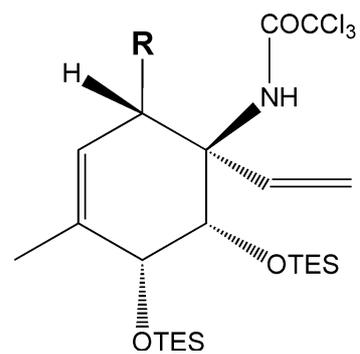
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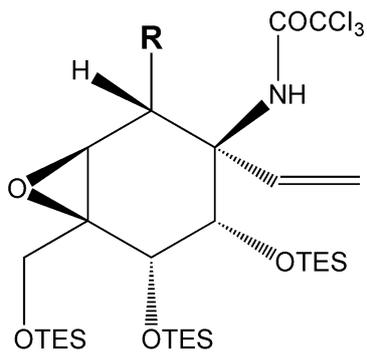
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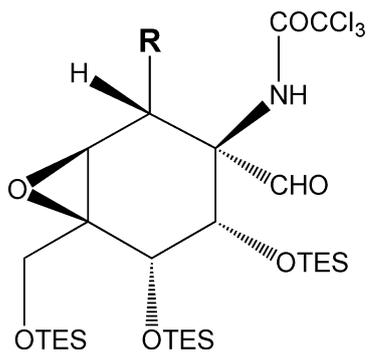
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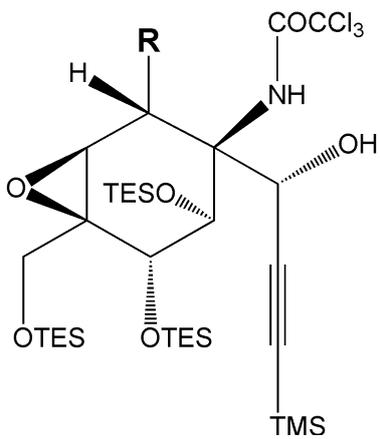
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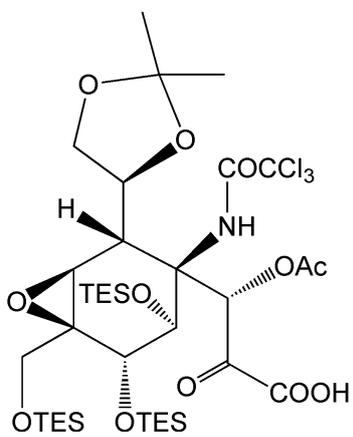


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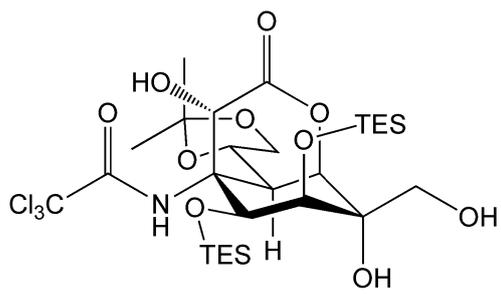


4.

21



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# Appendix

## Practical Tasks

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

1.

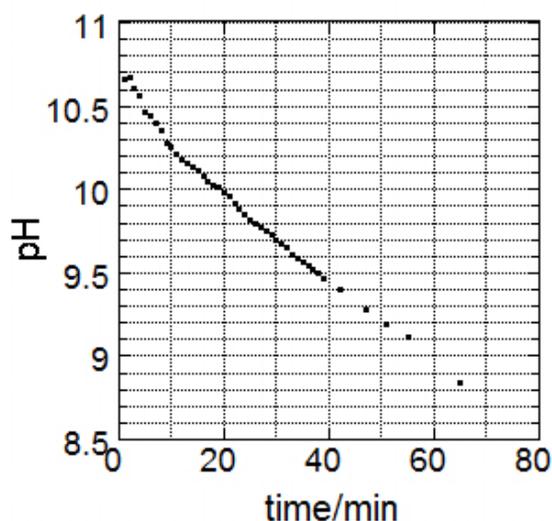
$C_1$ [mol L <sup>-1</sup> ]	$C_2$ [mol L <sup>-1</sup> ]
When 88.1 mg of ethyl acetate is used: $C_1 = \frac{88.1 \times 10^{-3} \text{ g} / 88.1 \text{ g mol}^{-1}}{0.100 \text{ L}}$ $= 0.0100 \text{ mol L}^{-1}$	When the concentration of aqueous solution of NaOH is 0.05005 mol L <sup>-1</sup> : $C_2 = 0.05005 \times \frac{2}{100}$ $= 0.001001 \text{ mol L}^{-1}$



3.

Time (minutes)	Temperature (°C)	pH	Time (minutes)	Temperature (°C)	pH
5		10.46	35		9.56
10		10.26	40		9.45
15		10.11	47		9.28
20		9.81	51		9.19
25		9.82	55		9.11
30		9.70	65		8.84

4.



The slope is  $-2.642 \times 10^{-2} \text{ min}^{-1}$ .

$$-2.642 \times 10^{-2} \text{ min}^{-1} = -\frac{k'_1}{2.303}$$

Therefore,  $k'_1 = 6.084 \times 10^{-2} \text{ min}^{-1}$

5. The concentration of ethyl acetate after mixing is  $0.0100 \text{ mol L}^{-1} / 2 = 0.00500 \text{ mol L}^{-1}$

$$k'_1 = k_2 [\text{CH}_3\text{COOC}_2\text{H}_5]$$

$$k_2 = 6.084 \times 10^{-2} \text{ min}^{-1} / 0.00500 \text{ mol L}^{-1} = 13.61 \text{ mol}^{-1} \text{ L min}^{-1}$$

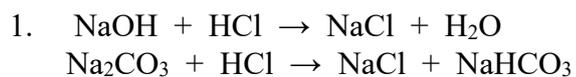
6.

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

$$-\ln \frac{1}{2} = 6.084 \times 10^{-2} \text{min}^{-1} \times t_{1/2}$$

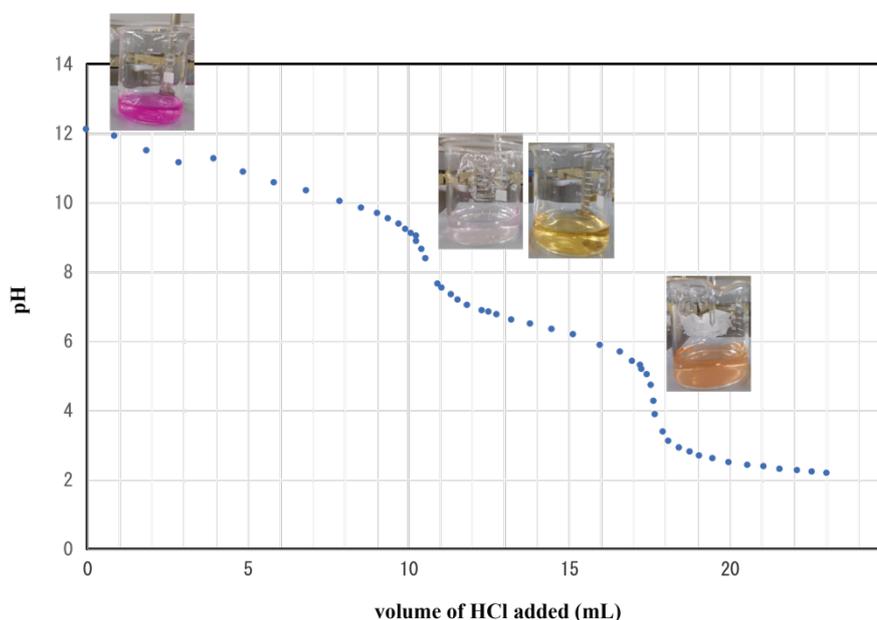
$$t_{1/2} = 0.6931 / 6.084 \times 10^{-2} \text{min}^{-1} = 11.39 \text{ min}$$

## Task 2. Simultaneous acid–base titration



3.  $\text{NaOH} \text{ [g]} : 0.0040 \times (V_a - V_b) / \frac{20}{1000} \text{ [g]}$   
 $\text{Na}_2\text{CO}_3 \text{ [g]} : 0.0053 \times 2 \times (V_b) / \frac{20}{1000} \text{ [g]}$

4. The horizontal axis is the amount of the standard solution added, while the vertical axis is the pH value of the unknown alkali solution. The following figure shows the actual measurement data (unknown alkali solution: 30.00 mL) where the unknown alkali solution was prepared from 1.0 L distilled water containing 0.5 g of NaOH and 2.5 g of  $\text{Na}_2\text{CO}_3$ .



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

1-4 The concentration of the potassium permanganate aqueous solution  $c$  is given by

$$c = \frac{w \times 2 / 134 / 5}{v \times 1000}$$

where  $w$  is the weight of sodium oxalate used in step B-1 and  $v$  is the volume of the aqueous potassium permanganate solution (accepted) used in the titration in step B-1.



3. The weight% of the oxalate ion is given by

$$c \times x / 1000 \times 5 / 2 \times 88 / y \times 100$$

where  $c$  is the concentration of the potassium permanganate aqueous solution determined above,  $x$  is the volume of the potassium permanganate aqueous solution (accepted) used in the titration in step B-2 and  $y$  is the weight of cobalt oxalate complex analyzed in step B-2.

From the table below, if the weight% of oxalate ion is more than 50.8% ( $= (53.4 + 48.3) / 2$ ), the product can be estimated to be a tris complex. Thus, cobalt ion to oxalate ligand composition ratio is 1:3.

<u>Compound composition</u>	<u>Molecular weight</u>	<u>Weight% of oxalate ion</u>
tris complex: $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	494.3	53.4 %
bis complex: $\text{K}[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$	364.1	48.3 %
mono complex: $[\text{Co}(\text{C}_2\text{O}_4)\text{Cl}(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$	290.5	30.3 %

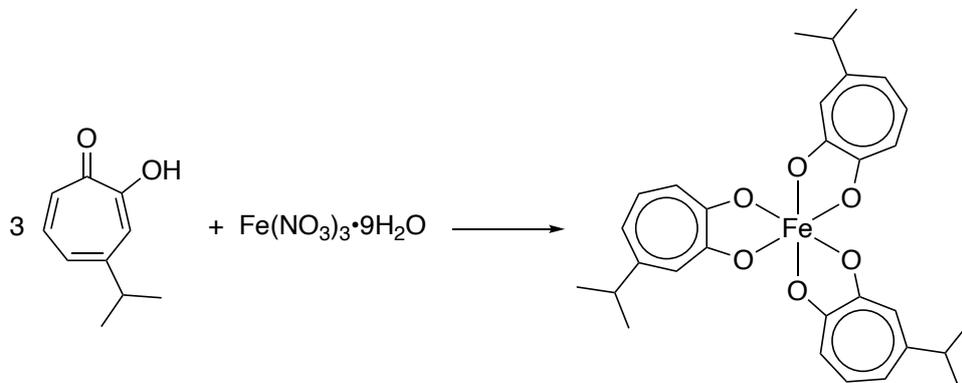
4. The molecular weight of cobalt(II) chloride hexahydrate is 238 g/mol. If it is estimated that a tris complex was formed, the yield is given by

$$z / 494.3 \times 238 \times 100$$

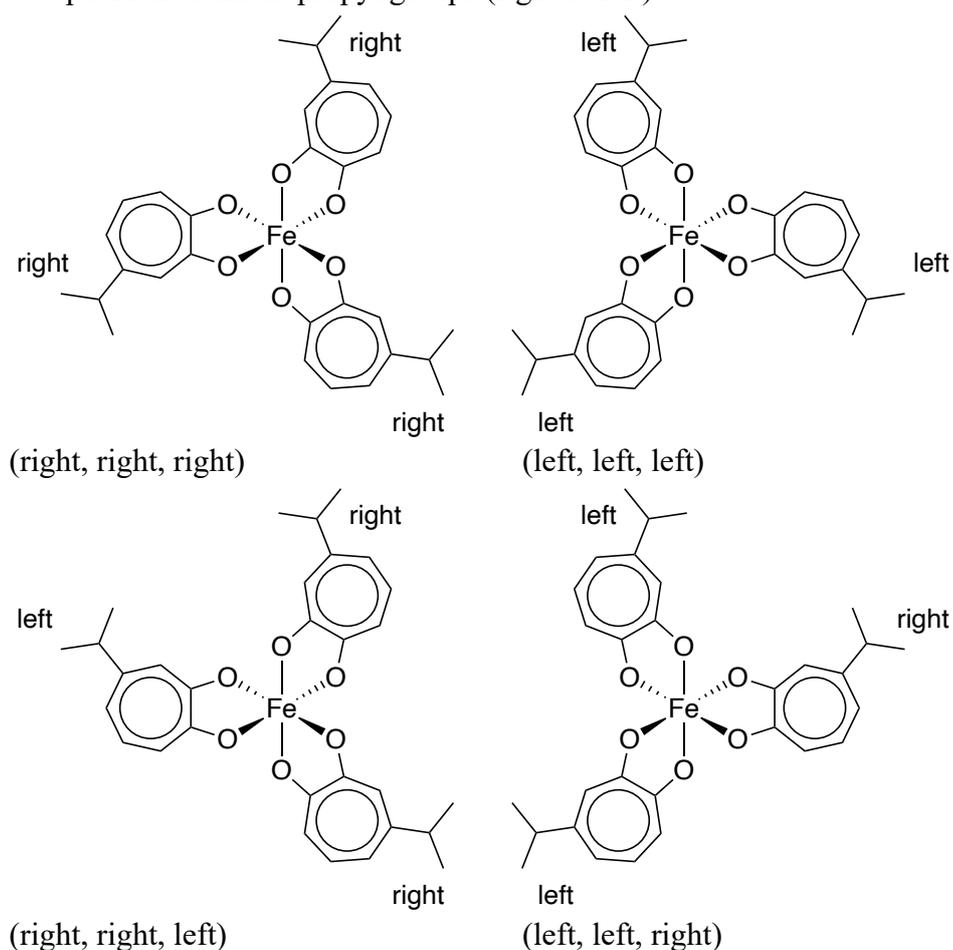
where  $z$  is the weight of the crystals of the complex obtained in step A.

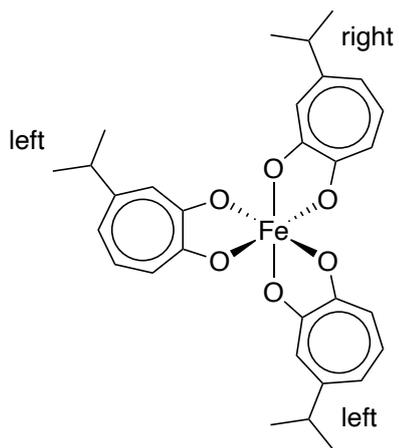
#### Task 4. Hinokitine: synthesis of a deep-red-colored natural product

- Hinokitine is a 3:1 complex of hinokitiol and iron(III) ion with the molecular formula (MF)  $C_{30}H_{33}FeO_6$  and a molecular weight (MW) of  $545.43 \text{ g mol}^{-1}$ . The theoretical yield of hinokitine can be calculated from the amounts of the reactants hinokitiol (MF =  $C_{10}H_{12}O_2$  and MW = 164.20) and iron(III) nitrate nonahydrate (MF =  $FeH_{18}N_3O_{18}$  and MW = 403.99) used in the synthesis.

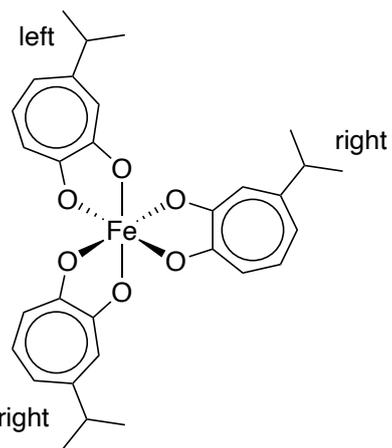


- Nitric acid ( $HNO_3$ )
- There are 8 isomers in total, including enantiomers ( $\Delta$  and  $\Lambda$ ) of hinokitine, depending on the position of the isopropyl groups (right or left)

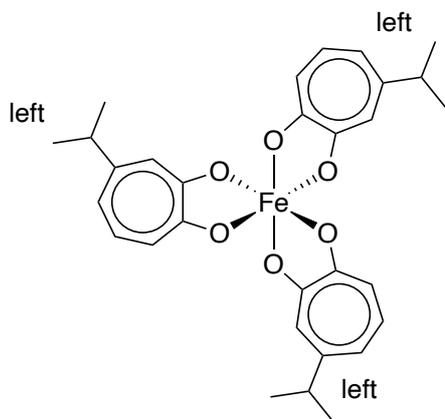




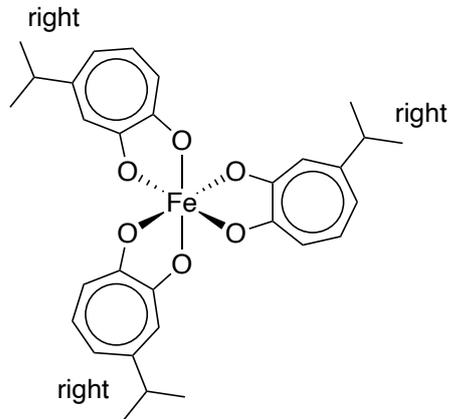
(right, left, left)



(left, right, right)



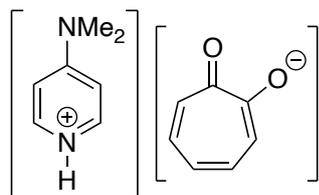
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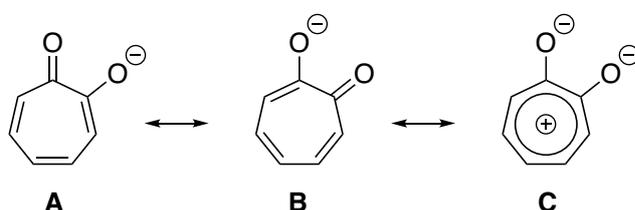
(right, right, right)

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

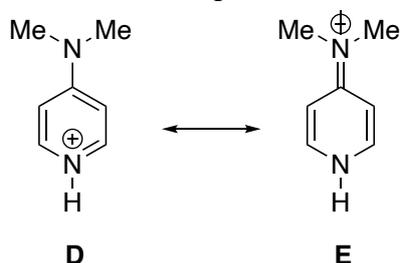
1.



4-Dimethylaminopyridine (DMAP) acts as a Brønsted base in this reaction. A tropolonate salt, 4-dimethylaminopyridinium tropolonate, is formed by proton transfer from the hydroxy group of tropolone to the nitrogen atom of the pyridine ring of DMAP. Tropolonate has an aromatic nature originating from the contribution of the canonical form with a tropylium ion structure (C).

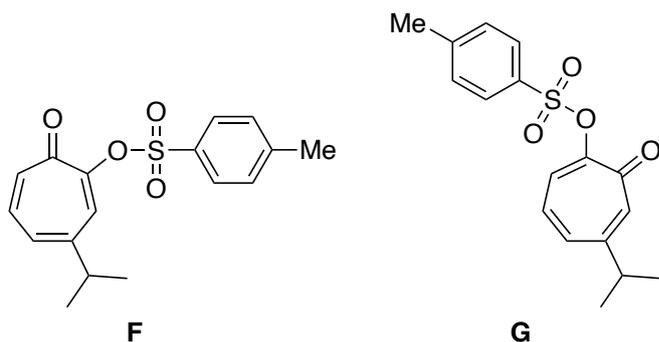


DMAP is more basic than pyridine due to the electron-donating effect of the dimethylamino group at the 4-position. The dimethylamino group can stabilize the positive charge on the protonated DMAP with the possible resonance structure (E).

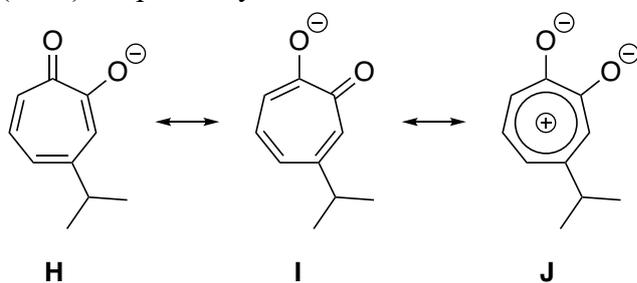


2. After the tosylation, DMAP is transformed into DMAP hydrochloride, [(DMAP)H][Cl], which is soluble in water. The typical procedure for the recovery of DMAP is as follows. An appropriate organic solvent and water are added to the reaction mixture. While the organic layer mainly contains tropolone tosylate, the aqueous layer contains the DMAP hydrochloride. The aqueous layer is basified with an aqueous solution of sodium hydroxide (NaOH) followed by extraction into an appropriate organic solvent. The organic layer is dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under vacuum to afford solid DMAP. Sufficiently pure DMAP can be obtained using a further purification technique, such as crystallization from an appropriate organic solvent or chromatography on silica gel using an appropriate organic solvent as the eluent.

3.

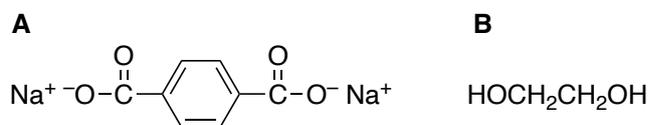


There are two tosylation products of hinokitiol (**F** and **G**), which are isomers. Hinokitiol is deprotonated by DMAP in a fashion similar to tropolone, affording the isopropyl-substituted tropolonate with three possible resonance forms (**H**, **I**, and **J**, which are analogous to **A**, **B**, and **C**). The products **F** and **G** are formally obtained from the reaction of **H** and **I** with tosyl chloride (TsCl), respectively.



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

1.



2. The theoretical weight of A can be calculated using the following equation:

$$\begin{aligned} \text{Theoretical weight of A} &= 1.00 \text{ [g]} * \frac{\text{molecular weight of disodium terephthalate}}{\text{formula weight of the repeating unit of PET}} \\ &= 1.00 \text{ [g]} * \frac{210.09}{192.17} = 1.09 \text{ [g]} \end{aligned}$$

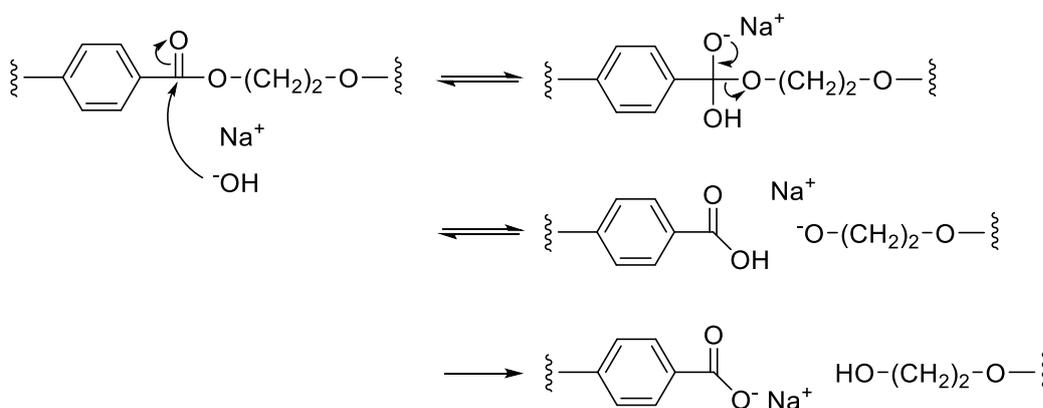
The yield of A based on the amount of PET used can be calculated using the following equation:

$$\text{Theoretical yield of A [\%]} = \frac{\text{weight of A obtained}}{\text{theoretical weight of A}} * 100$$

3. The yield of A based on the amount of PET reacted can be calculated using the following equation:

$$\text{Theoretical yield of A [\%]} = \frac{\text{weight of A obtained}}{\text{theoretical weight of A} * \frac{\text{weight of PET reacted}}{\text{weight of PET used}}} * 100$$

4.



5. As shown above, the first and the second steps are reversible. On the other hand, the final step is not reversible, because the neutralization reaction between the acidic carboxyl group and the highly basic alkoxide gives a carboxylate, which is not sufficiently basic to regenerate the alkoxide by deprotonation of the hydroxyl group. The irreversible nature of the final step makes the overall system irreversible. In addition, the hydroxyl group, which is much less nucleophilic than the alkoxide, is not able to attack the carbonyl group to induce the backward condensation reaction. Another reason is the poor solubility of the resulting disodium terephthalate, which precipitates from solution, which shifts the equilibrium toward the formation of the products.

6. Under the same conditions, the hydrolysis conducted in this experiment is much more efficient than the hydrolysis of the polyamide. The carbonyl carbon atom of the amide group is less electrophilic than that of the ester group on account of the greater extent of delocalization of the lone pair on the nitrogen atom compared to the lone pair on the oxygen. Consequently, the carbonyl carbon atom of the amide group is more resistant to the nucleophilic addition of the hydroxide ion than the ester group. Moreover, even if the nucleophilic addition of the hydroxide ion ( $\text{OH}^-$ ) took place, the resulting intermediate would preferentially release  $\text{OH}^-$  rather than the amide anion ( $\text{NHR}^-$ ), which is much more basic than  $\text{OH}^-$  and thus more difficult to produce. In other words, the intermediate preferentially dissociates to recover the amide bond.

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

1. 4-(phenylazo)phenol  
Recrystallization is effective or available when (1) the desired compound is major in the mixture and when (2) the desired compound is more easily crystallized than the impurity. The recrystallization of the 'mixture' for the column chromatography (1:1 mixture) to separate 4-(phenylazo)phenol will be unsuccessful.
2. Guaiazulene from the first colored fraction (blue) and 4-(phenylazo)phenol from the second colored fraction (orange).
3. Recrystallization is conducted by the difference of solubility at different temperatures. Although the solubility of the substance would decrease at lower temperature, it does not drop to zero. Because of some solubility of the substance at lower temperature, the yield of recrystallization cannot be quantitative.
4. Guaiazulene eluted first, and 4-(phenylazo)phenol eluted later. This means that 4-(phenylazo)phenol exhibits higher interaction (affinity) with the stationary phase, silica gel. The hydroxy group interacts with the OH group on the surface of the silica gel via hydrogen bonding. Nitrogen atoms in 4-(phenylazo)phenol may also contribute the interaction, although the basicity of  $sp^2$  nitrogen is low, and strong interaction is not expected from the azo group. It should be noted the azobenzene itself is a neutral compound, and exhibits low affinity with silica gel.

53<sup>rd</sup> IChO2021 Preparatory Problem version 2.5  
Edited by Nobuhiro Kihara, Kanagawa University  
version 2.0: Issued at 1<sup>st</sup> February, 2021.  
version 2.1: Issued at 15<sup>th</sup> February, 2021.  
version 2.2: Issued at 15<sup>th</sup> March, 2021.  
version 2.3: Issued at 29<sup>th</sup> March, 2021.  
version 2.4: Issued at 7<sup>th</sup> April, 2021.  
version 2.5: Issued at 8<sup>th</sup> June, 2021.  
final version: Issued at 12<sup>th</sup> July, 2021.

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