Preparatory Problems

Solutions to the tasks

"Bonding the World with Chemistry"

49th INTERNATIONAL CHEMISTRY OLYMPIAD
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Task lists

Solution to the Tasks

Task 1. Dimerization of Acetic Acid

1.1) The reaction can be represented as $2CH_3COOH \rightleftharpoons (CH_3COOH)_2$.
If we begin with, say, 100.0 mol CH_3COOH and 92.0% dimerizes, then 8.0 mol will be present at equilibrium. The 92.0 mol that react give rise to 46.0 mol dimers. The total number of moles present is therefore 54.0. Hence using the data at 298 K, the equilibrium constant, K_p, is given by

$$K_p = \frac{P_{(CH_3COOH)_2}}{(P_{CH_3COOH})^2} = \frac{X_{(CH_3COOH)_2} P_{tot}}{(X_{CH_3COOH} P_{tot})^2} = \frac{(46.0/54.0)(0.200)}{[(8.0/54.0)(0.200]^2} = 194$$

From equation $\Delta G^o = -RT \ln K_p$,

At 298 K, $\Delta G^o = -RT \ln K_p$

$= -(8.314 \text{ J K}^{-1}\text{mol}^{-1})(298 \text{ K}) \ln (194)$

$= -13.0 \text{ kJ mol}^{-1}$

At 318 K, $\Delta G^o = -RT \ln K_p$

$= -(8.314 \text{ J K}^{-1}\text{mol}^{-1})(318 \text{ K}) \ln (37.3)$

$= -9.57 \text{ kJ mol}^{-1}$

Applying the equation $\Delta G^o = \Delta H^o - T\Delta S^o$:
The method for the calculation is to write the two equations

$$\Delta G^o(298 \text{ K}) = -13.0 \text{ kJ mol}^{-1} = \Delta H^o - (298)\,\Delta S^o$$
$$\Delta G^o(318 \text{ K}) = -9.57 \text{ kJ mol}^{-1} = \Delta H^o - (318)\,\Delta S^o$$

and solve the equations simultaneously.
Then $\Delta H^o = -64.1 \text{ kJ mol}^{-1}$ and $\Delta S^o = -170 \text{ J K}^{-1} \text{ mol}^{-1}$.

1.2) Applying the Le Chatelier's principle, an increase of pressure should

✓ favor the dimerization.
○ not favor the dimerization.

1.3) The extent of dimerization

✓ decreases with increasing the temperature.
○ increases with increasing the temperature.

Task 2. Solubility of Calcite

According to $\Delta G^o_{sol} = -RT \ln K_{sp} = \Delta H^o_{sol} - T\Delta S^o_{sol}$,

we have $\ln K_{sp} = -\Delta H^o_{sol}/(RT) + \Delta S^o_{sol}/R$.

Assuming that ΔH^o_{sol} and ΔS^o_{sol} are temperature-independent,

$\ln (K_{sp1}/K_{sp2}) = -\Delta H^o_{sol}/R\ (1/T_1 - 1/T_2)$

$\ln (9.50/2.30) = -\Delta H^o_{sol}/R\ (1/273 - 1/323)$

Solving this equation to get $\Delta H^o_{sol} = -21$ kJ mol^{-1}.

Task 3. Expansion of Ideal Gas and Thermodynamics of Liquid Mixing

3.1) $\Delta U = 0$, $q = -w$

$w = -(1.00 \text{ atm})(2.42-0.200 \text{ dm}^3)(101.325 \text{ J dm}^{-3} \text{ atm}^{-1})$

$= -225$ J

$q = 225$ J

$\Delta S_{surr} = -225 \text{ J}/295.4 \text{ K} = -0.762 \text{ J K}^{-1}$

$\Delta S_{sys} = [(0.100 \text{ mol})(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) (295.4 \text{ K}) \ln(2.42 \text{ dm}^3/0.200 \text{ dm}^3)]/(295.4 \text{ K}) = 2.07 \text{ J K}^{-1}$

$\Delta S_{univ} = 2.07 + (-0.762) = 1.31 \text{ J K}^{-1}$

3.2) $\Delta H^{mix} = \Delta V^{mix} = 0$

The other functions are given by these equations:

$\Delta G^{mix} = RT\sum_i x_i \ln x_i$ and $\Delta S^{mix} = -R\sum_i x_i \ln x_i$.

The mole fraction of **A** is 3.00/(3.00+5.00) = 0.375.

The mole fraction of **B** is 1.000-0.375 = 0.625.

$\Delta G^{mix} = (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.0 \text{ K})\{0.375\ln(0.375)+0.625\ln(0.625)\} = -1639 \text{ J mol}^{-1}$

$\Delta S^{mix} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})\{0.375\ln(0.375)+0.625\ln(0.625)\} = 5.50 \text{ J K}^{-1} \text{ mol}^{-1}$

Task 4. Vibrational Frequency of a Diatomic Molecule

4.1) To find the reduced mass of CX, μ_{CX}:

$$E_0 = \left(0+\frac{1}{2}\right)h\nu \quad = \frac{1}{2}h\nu$$

$$E_1 = \left(1+\frac{1}{2}\right)h\nu \quad = \frac{3}{2}h\nu$$

$$\Delta E = E_1 - E_2 = \left(\frac{3}{2}-\frac{1}{2}\right)h\nu \quad = h\nu$$

$$\Delta E = hc\left(\frac{1}{\lambda}\right) = h\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad ;\ \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$c\left(\frac{1}{\lambda}\right) = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$k = 4\pi^2 c^2 \mu\left(\frac{1}{\lambda}\right)^2$$

$$\mu = \frac{k}{4\pi^2 c^2\left(\frac{1}{\lambda}\right)^2}$$

$$\mu = \frac{1.903\times10^3}{4(3.14)^2(2.9979\times10^{10}\,cm\cdot s^{-1})^2\left(2170.0\ cm^{-1}\right)^2}$$

$$\mu = 1.140\times10^{-26}\ \text{kg} = 6.866\ \text{amu}$$

$$\mu = 6.866\ \ \text{amu}$$

4.2) To find mass of the atom X, m_X:

$$\mu_{CX} = \frac{m_C m_X}{m_C + m_X}$$

$$\mu_{CX}(m_C + m_X) = m_C m_X$$

$$\mu_{CX} m_C + \mu_{CX} m_X = m_C m_X$$

$$m_C m_X - \mu_{CX} m_X = \mu_{CX} m_C$$

$$m_X = \frac{\mu_{CX} m_C}{m_C - \mu_{CX}}$$

$$m_x = \frac{6.866\times12.011}{12.011-6.866} = \frac{82.47}{5.145} = 16.03$$

Thus, atom X should be <u>oxygen</u>.

Task 5. Water-gas-shift Reaction

5.1) The mole fraction of H_2 in the reactor, $X_{H_2} = \dfrac{n_{H_2}}{n_{H_2} + n_{CO_2} + n_{H_2O} + n_{CO}} = \dfrac{0.475}{1.0} = 0.475$.

Thus, $P_{H_2} = X_{H_2} P_{total}$ = (0.475)(1.00 atm) = 0.475 atm.

And likewise, P_{CO_2} = 0.475 atm and $P_{H_2O} = P_{CO}$ = 0.025 atm

$$K = \frac{P_{H_2} P_{CO_2}}{P_{H_2O} P_{CO}} = \frac{(0.475)(0.475)}{(0.025)(0.025)} = 3.6 \times 10^2$$

Therefore, $\Delta G^o = -RT \ln K = -(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(273\ \text{K}) \ln(3.6 \times 10^2) = -13.4\ \text{kJ mol}^{-1}$.

5.2) The kinetics data given reflects the forward rate of the WGS reaction. The only rate law that is consistent with the given data is $r_f = k_f P_{CO} P_{H_2O}$, and $k_f = 4.4 \times 10^{-3}\ \text{atm}^{-1}\ \text{s}^{-1}$.

Thus, X = $(4.4 \times 10^{-3}\ \text{atm}^{-1}\ \text{s}^{-1})(0.28\ \text{atm})(0.72\ \text{atm}) = 8.9 \times 10^{-4}\ \text{atm s}^{-1}$.

5.3) $k_b = k_f/\text{K} = (4.4 \times 10^{-3}\ \text{atm}^{-1}\ \text{s}^{-1})/(3.6 \times 10^2) = 1.2 \times 10^{-5}\ \text{atm}^{-1}\ \text{s}^{-1}$.

So during the normal course of the reaction,

$r = r_f - r_b = k_f P_{CO} P_{H_2O} - k_b P_{CO_2} P_{H_2} = (4.4 \times 10^{-3}\ \text{atm}^{-1}\ \text{s}^{-1})(0.14\ \text{atm})(0.14\ \text{atm}) - (1.2 \times 10^{-5}\ \text{atm}^{-1}\ \text{s}^{-1})(0.36\ \text{atm})(0.36\ \text{atm}) = 8.44 \times 10^{-5}\ \text{atm s}^{-1}$.

5.4) $\Delta G = \Delta G^o + RT \ln Q = (-13.4\ \text{kJ mol}^{-1}) + (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(273\ \text{K}) \ln\left(\dfrac{(0.36)(0.36)}{(0.14)(0.14)}\right) = -9.1\ \text{kJ mol}^{-1}$

5.5) The reaction $CO_2H(ads) \rightarrow CO_2(ads) + H(ads)$ is first-order, whose rate can be expressed as rate = $k[CO_2H] = k\theta S_0 = k'\theta$, where S_0 denotes the maximum number of adsorbed intermediates for this surface.

Thus, θ= rate/k′ = $(1.0 \times 10^{11}\ \text{molecules s}^{-1}\ \text{cm}^{-2})/(2.0 \times 10^{12}\ \text{molecules s}^{-1}\ \text{cm}^{-2}) = 0.050$.

Task 6. Camphor in Benzene

$X_{ben} = n_{ben}/(n_{ben} + n_{cam})$
$n_{ben} = (100\ cm^3)(0.877\ g\ cm^{-3})(1\ mol/78.1\ g) = 1.12\ mol$
$n_{cam} = (24.6\ g)(1\ mol/152.2\ g) = 0.162\ mol$
$X_{ben} = (1.12\ mol)/(1.12\ mol + 0.162\ mol) = 0.874$
$P_{ben} = (X_{ben})(P^o_{ben}) = (0.874)(100\ torr) = 87.4\ torr$

$mass_{ben} = (100\ cm^3)(0.877\ g\ cm^{-3})(1\ kg/1000\ g) = 0.0877\ kg$

molality of camphor in solution = 0.162 mol camphor/0.0877 kg benzene = 1.85 mol kg^{-1}
$\Delta T = K_f\ m = (5.12\ ^oC\ kg\ mol^{-1})(1.85\ mol\ kg^{-1}) = 9.46\ ^oC$
Since pure benzene freezes at 5.50 ^oC, the solution will freeze at -3.96 ^oC.

Task 7. Gas and Liquid

7.1) According to the graph, the volume becomes zero at $T = -100\ ^oC$. This means that the absolute temperature should be calculated as T (K) = ^oC + 100 (not T (K) = ^oC + 273.15).

If $V_1 = 15\ cm^3$, $T_1 = -50\ ^oC + 100 = 50$ K, and $T_2 = 100\ ^oC + 100 = 200$ K, then we have
$(15\ cm^3/50\ K) = (V_2/200\ K)$.
Therefore, $V_2 = (15\ cm^3)(200\ K)/(50\ K) = 60\ cm^3$.

7.2) From Dalton's law, the total vapor pressure is the sum of the individual vapor pressures:

$$P_{total} = P_B + P_C \qquad (1)$$

Using the Raoult's law, the total pressure may be obtained by substituting each P term with $P_i^{\,o} \times X_i$, where $P_i^{\,o}$ is vapor pressure above pure liquid i and X_i is mole fraction of liquid i:

$$P_{total} = (P_B^o \times X_B) + (P_C^o \times X_C) \qquad (2)$$

We know from the question that there are 7 mol of liquid. We obtain the respective mole fractions X: the mole fraction of **B** is 3/7 and the mole fraction of **C** is 4/7.
Substituting values of X_i and $P_i^{\,o}$ into equation (2) yields the total pressure P_{total} as follows

$$P_{total} = (100.1\ kPa \times 3/7) + (60.4\ kPa \times 4/7)$$
$$= (42.9\ kPa) + (34.5\ kPa)$$
So $P_{total} = 77.4$ kPa

7.3) From the definition of mole fraction X, we say

$$X_{vaporB} = \frac{\text{moles of B in the vapor}}{\text{total number of moles in the vapor phase}}$$

The number of moles n_i are directly proportional to the partial pressure P_i if we assume that each vapor behaves as an ideal gas (we assume here that T and V are constant). Accordingly, we say

$$X_{vaporB} = \frac{\text{pressure of B}}{\text{total pressure}}$$

Substituting numbers from question 7.2:

$$X_{vaporB} = \frac{42.9\ \text{kPa}}{77.4\ \text{kPa}} = 0.554$$

The mole fraction of **B** in the vapor is 0.554, so it contains 55.4% **B**. The remainder of the vapor must be **C**, so the vapor also contains (100-55.4)% = 44.6% of **C**.

Note that the liquid phase comprises 43% **B** and 57% **C**, but the vapor contains proportionately more of the volatile **B**. We should expect the vapor to be richer in the more volatile component.

Task 8. Decomposition of Nitrous Oxide

8.1) Because the reaction is second order, therefore

$$\frac{1}{[N_2O]_t} - \frac{1}{0.108\ \text{mol dm}^{-3}} = (1.10 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})\ (1250\ \text{s})$$

$$[N_2O]_t = 0.0940\ \text{mol dm}^{-3}$$

8.2) Using Arrhenius equation,

$$\ln \frac{k_2}{1.10 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}} = -\frac{234 \times 10^3\ \text{J mol}^{-1}}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1}} \left[\frac{1}{873\ \text{K}} - \frac{1}{838\ \text{K}}\right]$$

$$k_2 = 4.23 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

Task 9. Avogadro's Number

9.1) Let $v = \alpha^3$, the volume of the unit cell

The number of unit cell in volume V of the silicon sphere = (V/v)

If n is the number of silicon atoms in the unit cell, the number of silicon atoms in silicon sphere = n(V/v)

The number of moles of Si in the sphere = (W/A)

The number of silicon atoms in sphere = moles x N_A.

i.e. $(W/A).N_A = n(V/v)$

$N_A = n(V/v).(A/W)$

9.2) For a face-centered unit cell, the number of atoms at the 8 corners of cell = 8; the number at the 6 faces = 6. Each corner has (1/8) of atom in unit cell and each face has (1/2) of atom. Thus total number of Si atoms in unit cell = 8x(1/8) + 6x(1/2) + 4 = 1 + 3 + 4 = 8.

n = 8

9.3) The volume v of the unit cell must be in unit of cm^3.

1 pm = 10^{-12} m = 10^{-10} cm

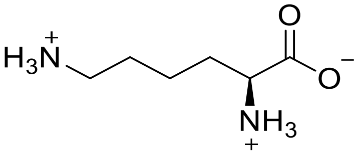
$N_A = 6.022\,141 \times 10^{23}$

Task 10. Buffer from Biological Acid: Lysine

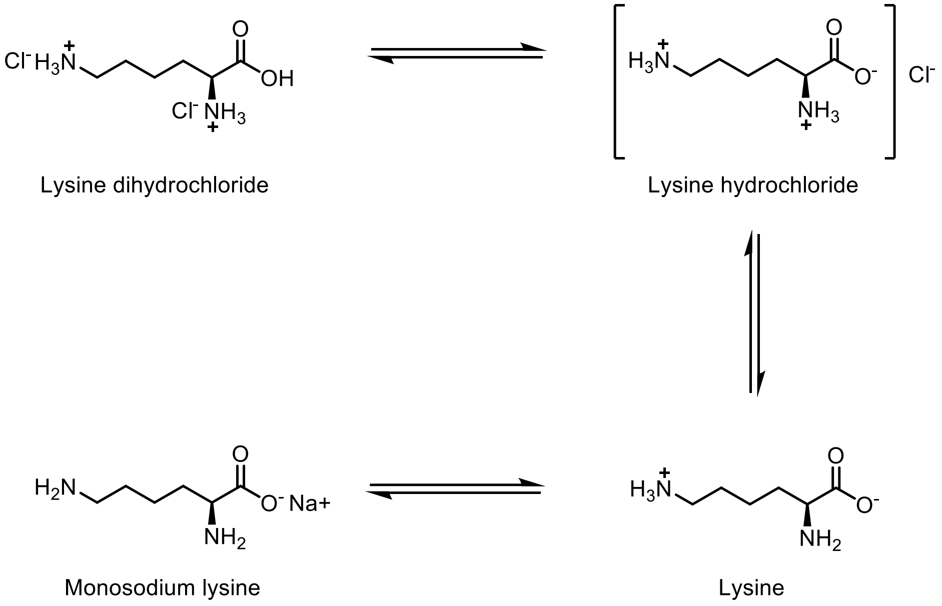
Acid Dissociation Constants

10.1)

No, the correct form is shown:



10.2)



10.3) *Given that* H_3L^{2+} *: the most acidic form*

H_2L^{+} *: the first intermediate form*

HL : the second intermediate form

L^{-}*: the most basic form*

$C_{H_3L^{2+}} = [H_3L^{2+}] + [H_2L^{+}] + [HL] + [L^{-}] = 0.1 \text{ mol dm}^{-3}$

total mol of H_3L^{2+} = *(0.100* mol dm^{-3}*)(0.1* dm^{3}*) = 0.01 mol*

total mol of H_3L^{2+} = (mol H_3L^{2+}) + (mol H_2L^{+}) + (mol HL) + (mol L^{-}) = 0.01 mol

At pH = 9.5, $[H^+] = 10^{-9.5}$ mol dm^{-3}

At pH = 9.5, the equilibrium moles of all forms can be calculated as follow;

mol H_3L^{2+} = total $\text{mol}_{H_3L^{2+}}\left(\frac{[H^+]^3}{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3}\right) = 1.14 \times 10^{-8}$ *mol (negligible)*

mol H_2L^{+} = total $\text{mol}_{H_3L^{2+}}\left(\frac{K_1[H^+]^2}{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3}\right) = 2.497 \times 10^{-3}$ mol

mol HL = total $\text{mol}_{H_3L^{2+}}\left(\frac{K_1K_2[H^+]}{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3}\right) = 6.88 \times 10^{-3}$ mol

mol L^- = total $\text{mol}_{H_3L^{2+}}(\frac{K_1K_2K_3}{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3})$ = 6.27 x 10^{-4} mol

Titration reaction to convert H_3L^{2+} to the desired forms;

$H_3L^{2+} + OH^- \rightarrow H_2O + H_2L^+$

$H_2L^+ + OH^- \rightarrow H_2O + HL$

$HL + OH^- \rightarrow H_2O + L^-$

mol of KOH required = (2.497 x 10^{-3}) + 2(6.88 x 10^{-3}) + 3(6.27 x 10^{-4})

= 1.814 x 10^{-2} mol

cm^3 of KOH required = = $(\frac{1000\ \text{cm3}}{0.5\ mol})(1.813 \text{ x } 10^{-2}\ mol) = 36.28$ cm^3

10.4) In this case, K_{a1} is carboxylic acid K_a, K_{a2} is ammonium K_a, and K_{a3} is substituent K_a.

HL is the second intermediate form

$[H^+] = \sqrt{\frac{K_{a2}K_{a3}[HL]+K_{a2}K_w}{K_{a2}+[HL]}}$

Since K_{a2} and K_{a3} are small;

$[HL] = \frac{(5.00\ g)\left(\frac{1\ mol}{146.19\ g}\right)}{0.100\ \text{dm}^3} = 0.342$ mol dm^{-3}

$[H^+] = \sqrt{\frac{[10^{-9.06}10^{-10.54}(0.342)]+[10^{-9.06}10^{-14})}{10^{-9.06}+0.342}} = 1.59x10^{-10}$ mol dm^{-3}

pH = 9.80

The alternative calculation is pH = (pK_{a2} + pK_{a3})/ 2 = (9.06 + 10.54)/2 = 9.80.

10.5) $HL \rightleftharpoons L^- + H^+$ $K_{a3} = 10^{-10.54}$

$HL + H_2O \rightleftharpoons H_2L^+ + OH^-$ $K_{b2} = \frac{K_W}{K_{a2}} = \frac{10^{-14}}{10^{-9.06}} = 1.15 \times 10^{-5}$

From question 10.4; $[H^+] = 1.59x10^{-10}$ mol dm^{-3}

$[OH^-] = \frac{K_W}{[H^+]} = \frac{10^{-14}}{1.59x10^{-10}} = 6.29 \times 10^{-5}$ mol dm^{-3}

At equilibrium;

$$[HL] = C_{HL}\left(\frac{K_1K_2[H^+]}{[H^+]^3+K_1[H^+]^2+K_1K_2[H^+]+K_1K_2K_3}\right)$$

Where; $C_{HL}=0.342$ M

[HL] = 0.250 M

$$K_{a3} = \frac{[L^-][H^+]}{[HL]}$$

$$\rightarrow [L^-] = \frac{K_{a3}[HL]}{[H^+]} = \frac{10^{-10.54}(0.250)}{1.59x10^{-10}} = 0.0453 \text{ mol dm}^{-3}$$

$$K_{b2} = \frac{[H_2L^+][OH^-]}{[HL]}$$

$$\rightarrow [H_2L^+] = \frac{K_{b2}[HL]}{[OH^-]} = \frac{1.15\times10^{-5}(0.25)}{6.29x10^{-5}} = 0.0457 \text{ mol dm}^{-3}$$

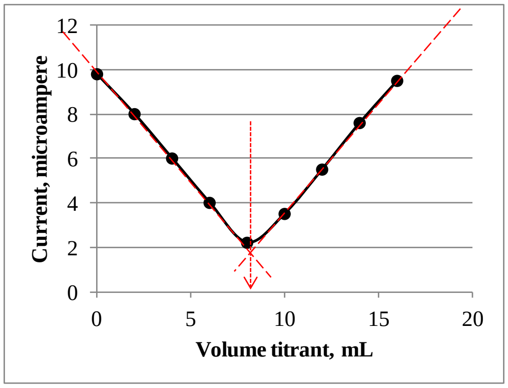
$$H_2L^+ + H_2O \rightleftharpoons H_3L^{2+} + OH^- \qquad K_{b3} = \frac{K_W}{K_{a1}} = \frac{10^{-14}}{10^{-2.16}} = 1.45\times10^{-12}$$

$$K_{b3} = \frac{[H_3L^{2+}][OH^-]}{[H_2L^+]}$$

$$\rightarrow [H_3L^{2+}] = \frac{K_{b3}[H_2L^+]}{[OH^-]} = \frac{1.45\times10^{-12}(0.0457)}{6.29x10^{-5}} = 1.05\times10^{-9} \text{ mol dm}^{-3}$$

Task 11. Amperometric Titration: Titration of Pb^{2+} with $Cr_2O_7^{2-}$

11.1) By extrapolating the two straight lines, the titration end-point is located.



11.2) $Pb^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightleftharpoons PbCr_2O_7(s)$

11.3) mol Pb = mol dichromate

0.0020 mol dm^{-3} x 8.0 cm^3 = 20.0 cm^3 x C_{lead}

Therefore, [lead] = 0.0020 x 8.0 / 20.0 = $8.0x10^{-4}$ mol dm^{-3}

Task 12. Conductometric Titration

12.1) The conductivity value before turning point comes from the mobility of H^+ and Cl^- from HCl. After NaOH was added to the titration vessel, the H^+ reacted with OH^- and the solution conductivity due to H^+ decreases. After the turning point, NaOH becomes excess in solution. The conductivity value increases with amount of added NaOH. The ion mobility of H^+ is higher than that of OH^-, hence the slope of titration curve before and after turning point is different.

12.2) From titration curve, the turning point is the end point, and is at 108 seconds.

Flow rate of NaOH = 3 drops / sec.

Therefore, the volume of NaOH is 108 x 3 = 324 drops = 324 x 0.029 cm^3 = 9.39 cm^3

The concentration of HCl = 9.39 x 0.100/ 25 = 0.037 mol dm^{-3}.

Task 13. Titration of Cu and Zn in Metal Alloy

13.1) $Cu_{(s)} + 4HNO_{3(aq)} \rightleftharpoons Cu^{2+} + 2NO_3^-{}_{(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

$Zn + 2HCl \rightleftharpoons Zn^{2+} + H_{2(g)} + 2Cl^-$

13.2) Total metal by EDTA titration = mol EDTA used = 33.4 x 0.1/1000 = 3.34×10^{-3} mol

Mol Cu by redox titration

$2Cu^{2+} + 4I^- \rightleftharpoons CuI(s) + I_2$

$I_2 + 2S_2O_3^{2-} \rightleftharpoons 2I^- + S_4O_6^{2-}$

mol Cu = mol thiosulfate used = 29.35x0.1/1000 = 2.935×10^{-3} mol

grams Cu = 2.935×10^{-3} mol x 63.5 = 0.1864 grams in 25.00 mL aliquot

Therefore, a 250 cm^3 sample solution will contain = 0.1864 x250/25 = 1.864 gram

Thus %w/w Cu = 1.864/2.300 x 100 = 81.0 %

mol Zn = total metal – Cu = $3.34 \times 10^{-3} - 2.935 \times 10^{-3} = 4.05 \times 10^{-4}$ mol

grams Zn = 4.05×10^{-4} mol x 65.4 = 2.649×10^{-2} grams in 25.00 aliquot

Therefore, 250 cm^3 sample solution will contain = 2.649×10^{-2} x250/25 = 0.2649 gram

Thus %w/w Zn = 0.2649/2.300 x 100 = 11.5 %

Task 14. Spectrophotometric Determination of Iron

14.1)

a) At $C_L = 2.20 \times 10^{-2}$ mol dm^{-3}, $[ML_3] = 6.25 \times 10^{-5}$

$A = \varepsilon bC$, therefore $\varepsilon = A/bC = 0.750/6.25 \times 10^{-5} = 12{,}000$ L mol^{-1} cm^{-1}

b) $M + 3L \rightleftharpoons ML_3$

$K_f = [ML_3] / [M] [L]^3$ (1)

at $C_L = 9.25 \times 10^{-5}$ M, $[ML_3] = 0.360 / 12000$

$[ML_3] = 3.0\times 10^{-5}$ mol dm^{-3} (2)

therefore, $[M] = (3.25 \times 10^{-5}) - (3.0\times 10^{-5})$

$[M] = 0.25 \times 10^{-5}$ mol dm^{-3} (3)

$[L] = (9.25 \times 10^{-5}) - 3 \times (3.0\times 10^{-5})$

$[L] = 0.25 \times 10^{-5}$ mol dm^{-3} (4)

Hence $K_f = (3.0\times 10^{-5}) / (0.25 \times 10^{-5}) (0.25 \times 10^{-5})^3$

$K_f = 7.68 \times 10^{17}$ dm^3 mol^{-3}

14.2) mole of C : mole of H : mole of N = 80/12 : 4.44/1 : 15.56/14

= 6.67 : 4.44 : 1.11

= 6 : 4 : 1

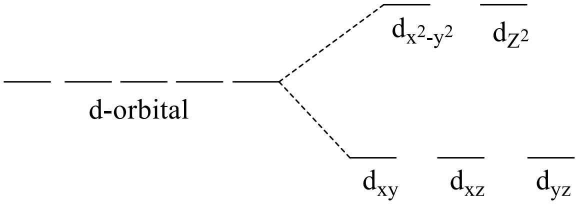
therefore, the empirical formula of L is C_6H_4N

The empirical molar mass = (6 x 12) + (4 x 1) + (1 x 14) = 90

molar mass/ empirical molar mass = 180 / 2

Therefore, the molecular formula of L is $C_{12}H_8N_2$.

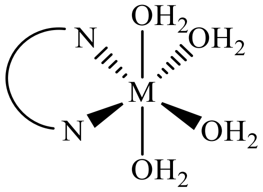
14.3) d-orbital splitting diagram for ML_3



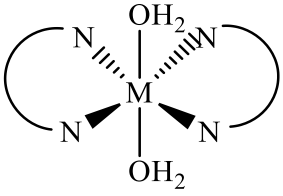
Octahedral field

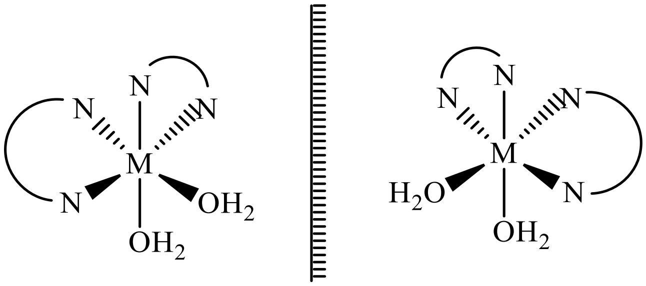
Possible isomers of Fe^{2+} complexes

ML :

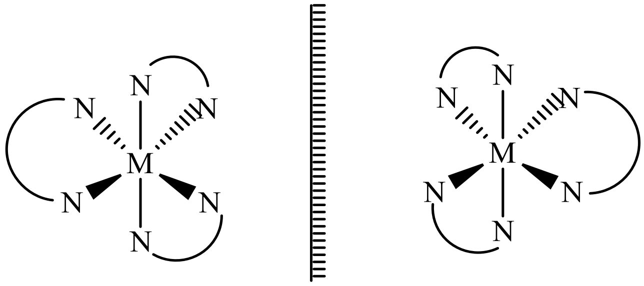


ML_2 :





ML_3 :



Δ_o of $ML < ML_2 < ML_3$ $\because$ H_2O is a weaker field ligand as compared with bipyridine.

14.4)

$A = \varepsilon bC$, therefore $C = A/\varepsilon b = 0.550/12000 = 4.58 \times 10^{-5}\ \text{mol dm}^{-3}$

The concentration of dialyzable iron is

$4.58 \times 10^{-5}\ \text{mol dm}^{-3} \times 50.00/5.00 \quad = 4.58 \times 10^{-4}\ \text{mol dm}^{-3}$

$4.58 \times 10^{-4}\ \text{mol dm}^{-3} \times 55.845\ \text{g mol}^{-1} \times 1000\ \text{mg g}^{-1} \quad = 25.58\ \text{mg dm}^{-3}$

14.5)

From 14.4), the concentration of dialyzable iron is 25.58 mg dm^{-3} which is also equal to the concentration of iron inside the dialysis bag.

The total volume is 12.50 cm^3 (inside the dialysis bag) + 20.00 cm^3 (outside the bag)

= 32.50 cm^3.

Therefore, the total amount of digestible iron is

$(25.58\ \text{mg dm}^{-3} \times 32.50\ \text{cm}^3) / (1000\ \text{cm}^3\ \text{dm}^{-3}) = 0.8314\ \text{mg}$

For the supplement of 0.4215 g, the iron content is 0.8314 mg

For the supplement of 1.0000 g, the iron content is 0.8314 mg x 1.0000 g / 0.4215 g

= 1.972 mg

Task 15. Basic Electrochemistry

15.1)

Anode: $Mn^{2+} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5e^-$

Cathode: : $5Ce^{4+} + 5e^- \rightleftharpoons 5Ce^{3+}$

Net : $Mn^{2+} + 4H_2O + 5Ce^{4+} \rightleftharpoons MnO_4^- + 8H^+ + 5Ce^{3+}$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = 1.70 - 1.507 = 0.193V$$

$$E^o_{cell} = \frac{0.05916}{n} \log K$$

$$0.193 = \frac{0.05916}{5} \log K$$

$$K = 2.05 \times 10^{16}$$

15.2)

$$5\ mg\ Ce^{4+}\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol\ Ce^{4+}}{140.12\ g\ Ce^{4+}}\right)\left(\frac{5\ mol\ e^{-}}{5\ mol\ Ce^{4+}}\right)\left(\frac{96{,}485\ C}{1\ mol\ e^{-}}\right) = 3.44\ C$$

15.3)

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{n}logQ$$

Where Q is a reaction quotient.

$$E_{cell} = E^{o}_{cell} - \frac{0.05916}{n}log[\frac{[MnO_4^-][H^+]^8[Ce^{3+}]^5}{[Mn^{2+}][Ce^{4+}]^5}]$$

$$E_{cell} = 0.193 - \frac{0.05916}{5}log[\frac{[0.001][.001]^8[0.01]^5}{[0.002][0.01]^5}]$$

$$E_{cell} = 0.481V$$

Task 16. Calculation of Concentration

16.1) mol Cu in $CuCl_2$ 1.345 g = 1.345 g/ (63.55 + 2(35.45) g mol^{-1}) = 0.0100 mol Cu

mol Cu in 50.00 cm^3 of $CuSO_4$ 31.9 g dm^{-3}

= (50 cm^3 /1000 cm^3 dm^{-3}) x (31.9 g dm^{-3} /159.62 g mol^{-1}) = 0.00999 mol Cu

Therefore, the total mol Cu is 0.0100 + 0.00999 = 0.01999 = 0.02 mol

500 cm^3 contains 0.02 mol Cu, therefore the concentration is 0.04 mol dm^{-3}.

16.2) The concentration of Cu in 100.0 cm^3

= (25.00 cm^3 / 100.0 cm^3) x 0.04 mol dm^{-3} = 0.01 mol dm^{-3} or 10^{-2} mol dm^{-3}

pH = 8.0, implying that $[OH^-] = 10^{-6}$ mol dm^{-3}

$[Cu^{2+}][OH^-]^2 = (10^{-2})(10^{-6})^2 = 10^{-14}$ which is greater than the $K_{SP(Cu(OH)_2)}$, i.e., 4.8×10^{-20}

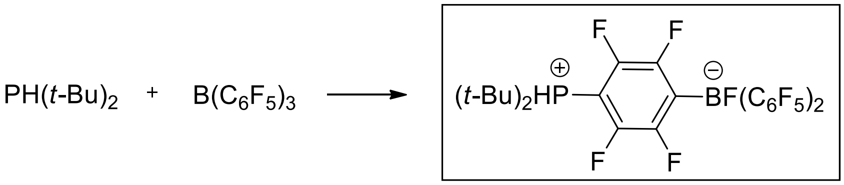
Therefore, the precipitate of $Cu(OH)_2$ is formed.

Task 17. Small Molecule Activation by Frustrated Lewis Pairs

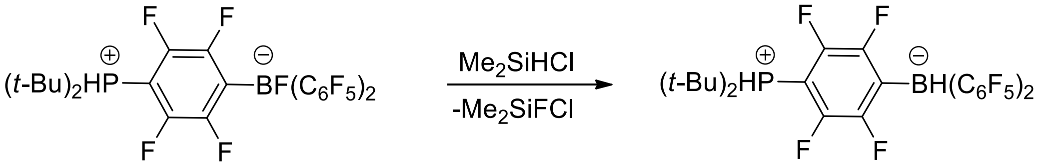
17.1)

$$C_6F_5Br \xrightarrow[\text{2. 1/3 BCl}_3]{\text{1. n-BuLi}} 1/3\ B(C_6F_5)_3$$

17.2)



17.3)



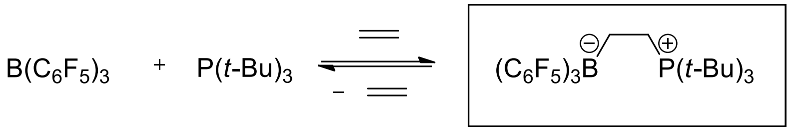
17.4)

$$B(C_6F_5)_3 \quad + \quad P(t\text{-Bu})_3 \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} \boxed{\left[\overset{\oplus}{H}P(t\text{-Bu})_3\right]\left[\overset{\ominus}{H}B(C_6F_5)_3\right]}$$

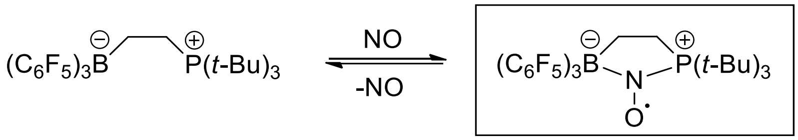
17.5)

$$B(C_6F_5)_3 \quad + \quad P(t\text{-Bu})_3 \underset{-HD}{\overset{HD}{\rightleftharpoons}} \boxed{\begin{array}{c}\left[\overset{\oplus}{D}P(t\text{-Bu})_3\right]\left[\overset{\ominus}{H}B(C_6F_5)_3\right] \\ + \\ \left[\overset{\oplus}{H}P(t\text{-Bu})_3\right]\left[\overset{\ominus}{D}B(C_6F_5)_3\right]\end{array}}$$

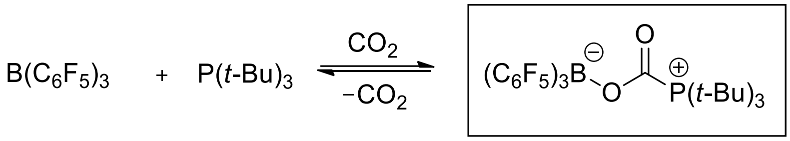
17.6)



17.7)



17.8)



Task 18. Silver Iodide

18.1) 0

The reduction of Ag^+ to Ag^0 causes the change of color.

18.2) AgF > AgCl > AgBr > AgI

The stronger interaction between Ag^+ and I^- as well as the low hydration energy of I^- result in the poor solubility of AgI. The smaller size of other halide ions led to poorer interaction with Ag^+; hence, higher solubility.

18.3) – 0.028 V

$$\Delta G^o = -nFE^o$$

For (a), $\Delta G^o_a = -(-1)(96{,}500)(0.80) = -77{,}200 \text{ J (mol Ag)}^{-1}$

$$\Delta G^o = -RT \ln K$$

For (c), $\Delta G^o_c = -(8.314)(298)(\ln 10^{14}) = -79{,}867 \text{ J mol}^{-1}$

The reduction half reaction of $[AgI_3]^{2-}$:

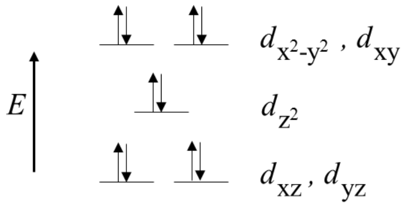
(d) $[AgI_3]^{2-}\,(aq) + e^- \rightleftharpoons Ag\,(s) + 3\,I^-\,(aq)$

Eqn (d) = (a) – (c)

Therefore, $\Delta G^{o}_{d} = \Delta G^{o}_{a} - \Delta G^{o}_{c} = -77{,}200 - (-79{,}867) = 2{,}667 \text{ J mol}^{-1}$

$E^{o} = -\Delta G^{o}_{d}/(nF) = -(2{,}667)/(96{,}500) = \underline{-0.028 \text{ V}}$

18.4) For trigonal planar,



The ligands lie in the xy plane, then the $d_{x^2-y^2}$ and d_{xy} orbitals that have their electron density concentrated in this plane will have the highest energy. The d_{xz} and d_{yz} orbitals have their electron density out of this xy plane, so their energies are the lowest. The d_{z^2} orbital has its electron density mostly out of the xy plane, but there is a ring of electron density in the xy plane, so the d_{z^2} orbital will have energy higher than the d_{xz} and d_{yz} orbitals but still lower than the $d_{x^2-y^2}$ and d_{xy} orbitals. In addition, the number of *d*-electrons for silver in $[AgI_3]^{2-}$ is 10. Therefore, all *d*-orbitals should be filled.

Task 19. Perovskite Structure

19.1) Number of Ca^{2+} ions: 8 corners x 1/8 ion Ca^{2+}/corner = 1

Number of O^{2-} ions: 6 cube faces x 1/2 O^{2-} ion/cube face = 3

Number of Ti^{4+} ions: one Ti^{4+} ion in the cube center = 1

Therefore, the empirical formula is $CaTiO_3$.

19.2) (1) octahedral hole (4 per unit cell), (2) tetrahedral hole (8 per unit cell)

19.3) Octahedral hole

Task 20. Quantum Numbers and Atomic Orbitals

20.1) (i) $l = n$ is not allowed. For a certain value of n, l can be any value from 0 to n-1 (i.e., less than n).

(ii) $m_l = -2$ is not possible for $l = 1$, because the magnitude of the m_l must not be greater than l. (For a certain value of l, $m_l = l,\ l-1, \ldots, -l$.)

(iii) $l = -1$ is not possible. l cannot have a negative value.

20.2) (i) 6*d*

(ii) 4*f*

(iii) 6*p*

20.3) (i) five

(ii) seven

(iii) one

Task 21. Radioactivitiy of Iodine and Nuclear Equations

21.1)

(i) After 2 half-lives, the remaining concentration of I-131 will be as follows:

$$[\text{I-131}] \qquad 0.1\ \text{mol dm}^{-3} \longrightarrow 0.05\ \text{mol dm}^{-3} \longrightarrow \boxed{0.025\ \text{mol dm}^{-3}}$$

(ii) After 40 days which is equal to 5 half-lives, the remaining concentration of I-131 will be as follows:

[I-131]

$$\begin{tikzcd}
0.1\ \text{mol dm}^{-3} \arrow[r] & 0.05\ \text{mol dm}^{-3} \arrow[r] & 0.025\ \text{mol dm}^{-3} \arrow[d] \\
\boxed{3.125 \times 10^{-3}\ \text{mol dm}^{-3}} & 6.25 \times 10^{-3}\ \text{mol dm}^{-3} \arrow[l] & 0.0125\ \text{mol dm}^{-3} \arrow[l]
\end{tikzcd}$$

21.2) (i) ${}^{14}_{6}\mathrm{C}$ (ii) ${}^{0}_{+1}e$ or β^+ (iii) ${}^{55}_{25}\mathrm{Mn}$ (iv) ${}^{238}_{92}\mathrm{U}$

(v) ${}^{1}_{0}\mathrm{n}$ (vi) ${}^{110}_{47}\mathrm{Ag}$ (vii) ${}^{96}_{39}\mathrm{Y}$ (viii) ${}^{4}_{2}\mathrm{He}$ or α

Task 22. Structure and Chemistry of Sodium Chloride

22.1) (i) 6 and 6

(ii) 4

(iii) 2.21 g cm^{-3}

Density = m/V

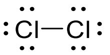
$V = a^3 = (560\ pm)^3 = 1.76 \times 10^{-22}\ cm^3$

$mass = (4 \times 58.5\ g)/(6.022 \times 10^{23}) = 3.89 \times 10^{-22}\ g$

Density = $3.89 \times 10^{-22}\ g / 1.76 \times 10^{-22}\ cm^3 = 2.21\ g\ cm^{-3}$

22.2) (i) $n = 3$, $l = 0$

(ii) Na is larger than Cl, but Cl^- is larger than Na^+.

(iii) 
$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$

(iv) -787 kJ mol^{-1}

$\Delta H_{\text{overall}} = -411\ kJ\ mol^{-1} = \Delta H_{\text{sublimation}}$ for Na + IE_1 for Na + ½(Cl-Cl dissociation) +

Electron affinity of Cl + lattice energy

$-411\ kJ\ mol^{-1} = 107\ kJ\ mol^{-1} + ½\ (224)\ kJ\ mol^{-1} + 496\ kJ\ mol^{-1} – 349\ kJ\ mol^{-1}$ + lattice energy

lattice energy = -787 kJ mol^{-1}

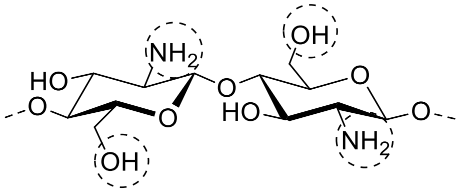
22.3) (i) $Br_2(l) + Cl^-(aq) \rightarrow$ no reaction

(ii) $Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$

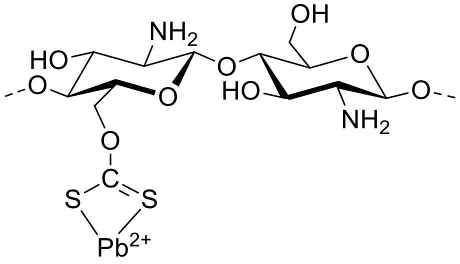
(iii) Yellow

Task 23. Natural Chelator from Shrimp Shell

23.1) The preferred binding sites are indicated in the circles as follows:

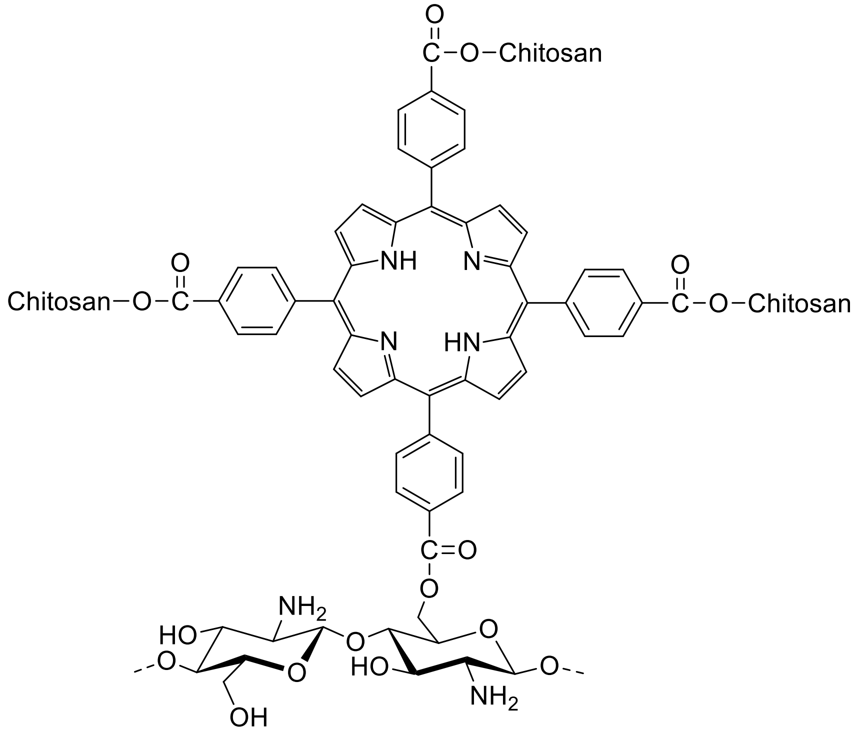


23.2)

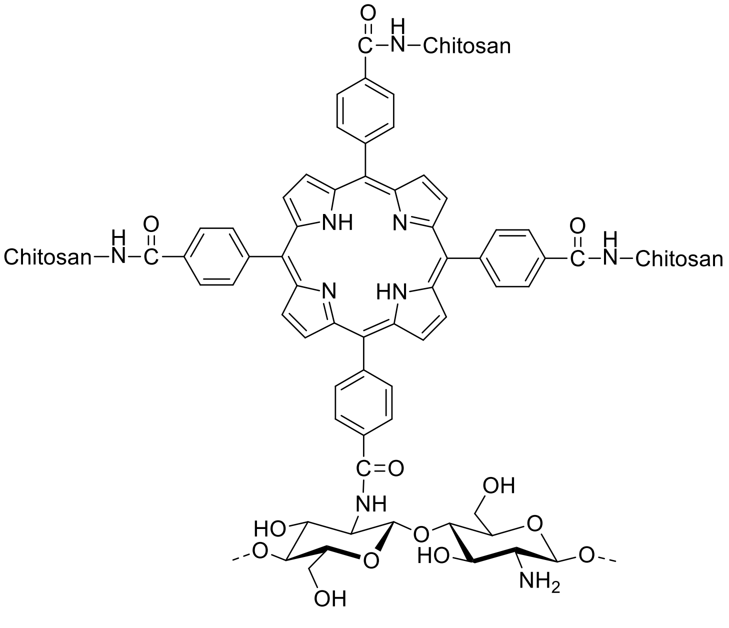


Pb^{2+} is a soft metal ion so it prefers to form bond with sulfur. This helps PMCS adsorb Pb^{2+} better.

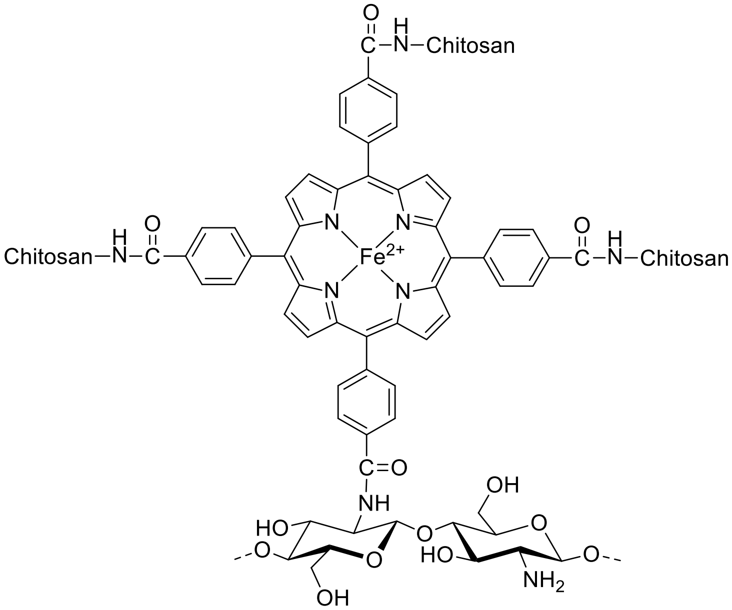
23.3) *meso*-tetra(*p*-carboxyphenyl)porphyrin can form ester bond with chitosan as shown in the proposed structure below:



Or amide bonds are formed as below:

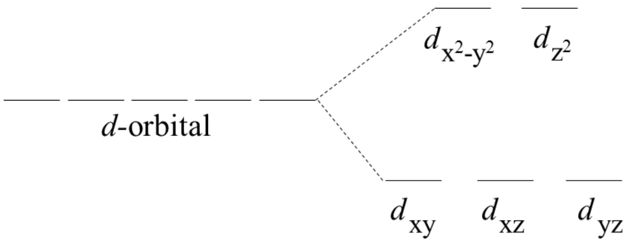


23.4) One of the structures in question 23.3 was chosen to bond with Fe^{2+} as the proposed structure below.



The two vacant axial sites are bonding with water molecules.

Assuming that the crystal fields are equivalent along the x, y, and z axes, the splitting diagram of Fe^{2+} *d* orbitals is shown below:



Octahedral field

Task 24. Compound Identification and Related Chemistry

24.1) **M**Cl_3 and **M** = Al

Theoretically, the maximum amount of the product is obtained when the mole fraction of **M** and Cl_2 are in the correct stoichiometric ratio. Based on the experiments, **M**:Cl_2 = 0.4:0.6 or 2/3 is the stoichiometric ratio needed to form $\mathbf{M}_xCl_y$. Thus, the equation is as follows:

$$2\ \mathbf{M} + 3\ Cl_2 \rightarrow 2\ \mathbf{M}Cl_3.$$

∴ the chemical formula of $\mathbf{M}_xCl_y$ = **M**Cl_3

Since 0.4 mole of M generates 0.4 mole of **M**Cl_3, the molar mass of **M**Cl_3 and atomic mass of M can be derived:

Molar mass of **M**Cl_3 = 53.3 g/0.40 mol = 133 g mol^{-1}

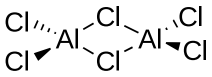
Atomic mass of **M** = 133 – (3 × atomic mass Cl) = 133.3 – (3 × 35.45) = 26.9 g mol^{-1}

∴ **M** = Al

24.2) (i) $AlCl_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3\ HCl$

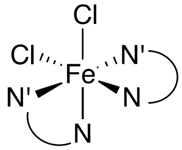
(ii) $2\ AlCl_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6\ HCl$

24.3)

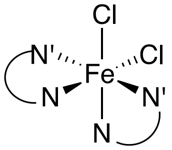


Task 25. Isomerism of Octahedral Fe(II) Complexes

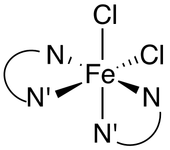
25.1)



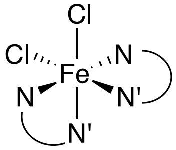
isomer **A**
cis(Cl,Cl)
trans(N',N'), *cis*(N,N)



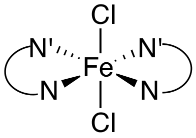
isomer **A***
cis(Cl,Cl)
trans(N',N'), *cis*(N,N)



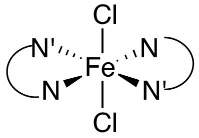
isomer **B**
cis(Cl,Cl)
cis(N',N'), *trans*(N,N)



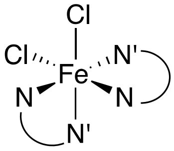
isomer **B***
cis(Cl,Cl)
cis(N',N'), *trans*(N,N)



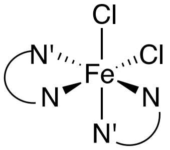
isomer **C**
trans(Cl,Cl)
cis(N',N'), *cis*(N,N)



isomer **D**
*trans(*Cl,Cl)
trans(N',N'), *trans*(N,N)



isomer **E**
cis(Cl,Cl)
cis(N',N'), *cis*(N,N)



isomer **E***
cis(Cl,Cl)
cis(N',N'), *cis*(N,N)

25.2) isomers **A**, **A***, **B**, **B***, **E**, and **E***

Task 26. Stoichiometry and Structure Determination

26.1) $C_9H_{10}O_3$

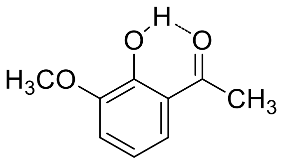
Solution: % by weight C : H : O = 65.0 : 6.10 : 28.9

% by mol C : H : O $= \frac{65.0}{12.0} : \frac{6.10}{1.01} : \frac{28.9}{16.0}$

$= 5.42 : 6.04 : 1.81$

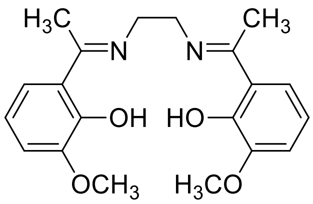
$\therefore$ empirical formula C : H : O = 9 : 10 : 3

26.2)

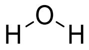


26.3)

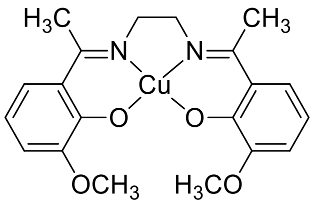
X =



Y =

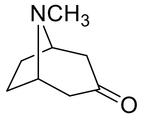


Z =

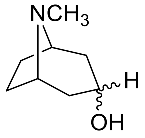


Task 27. Atropine

27.1)

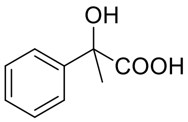


A
tropinone ($C_8H_{13}NO$)

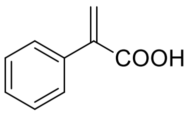


B
tropine ($C_8H_{15}NO$)

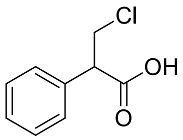
27.2)



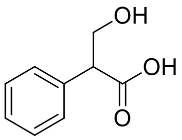
C



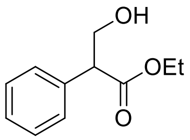
D



E

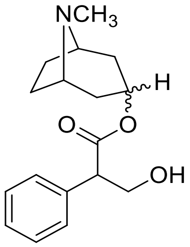


F
tropic acid ($C_9H_{10}O_3$)



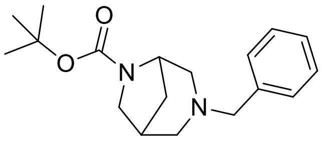
G

27.3)

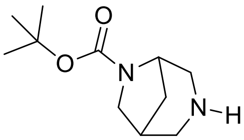


H: atropine

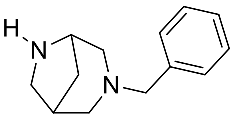
27.4)



I
$C_{18}H_{26}N_2O_2$



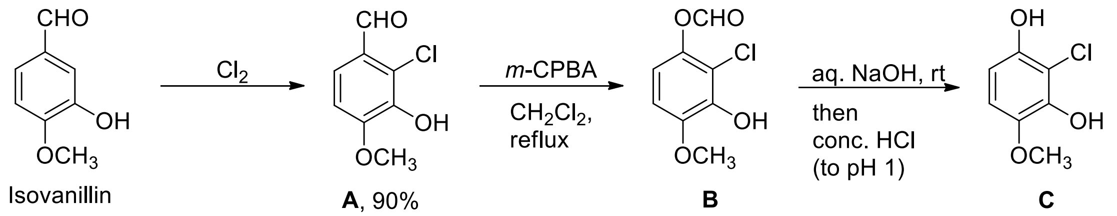
J

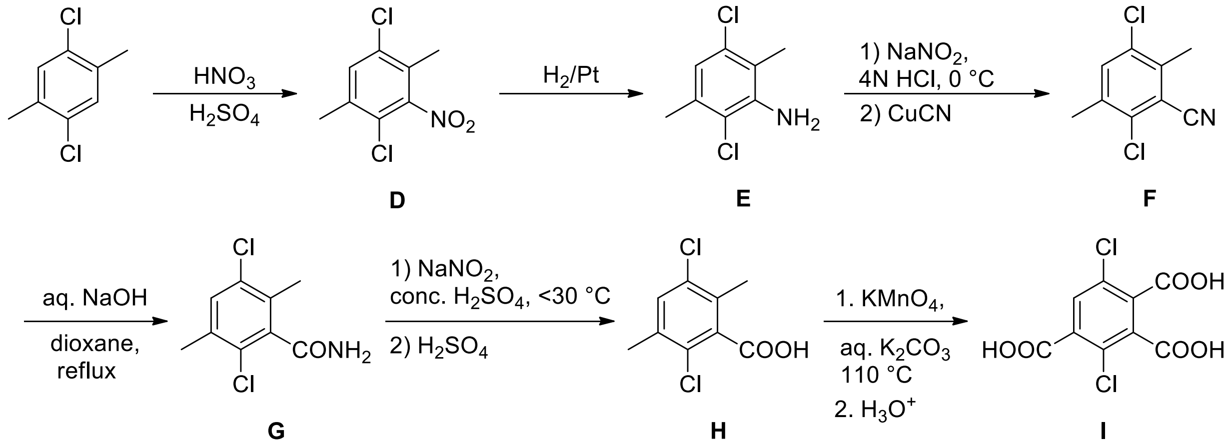


K

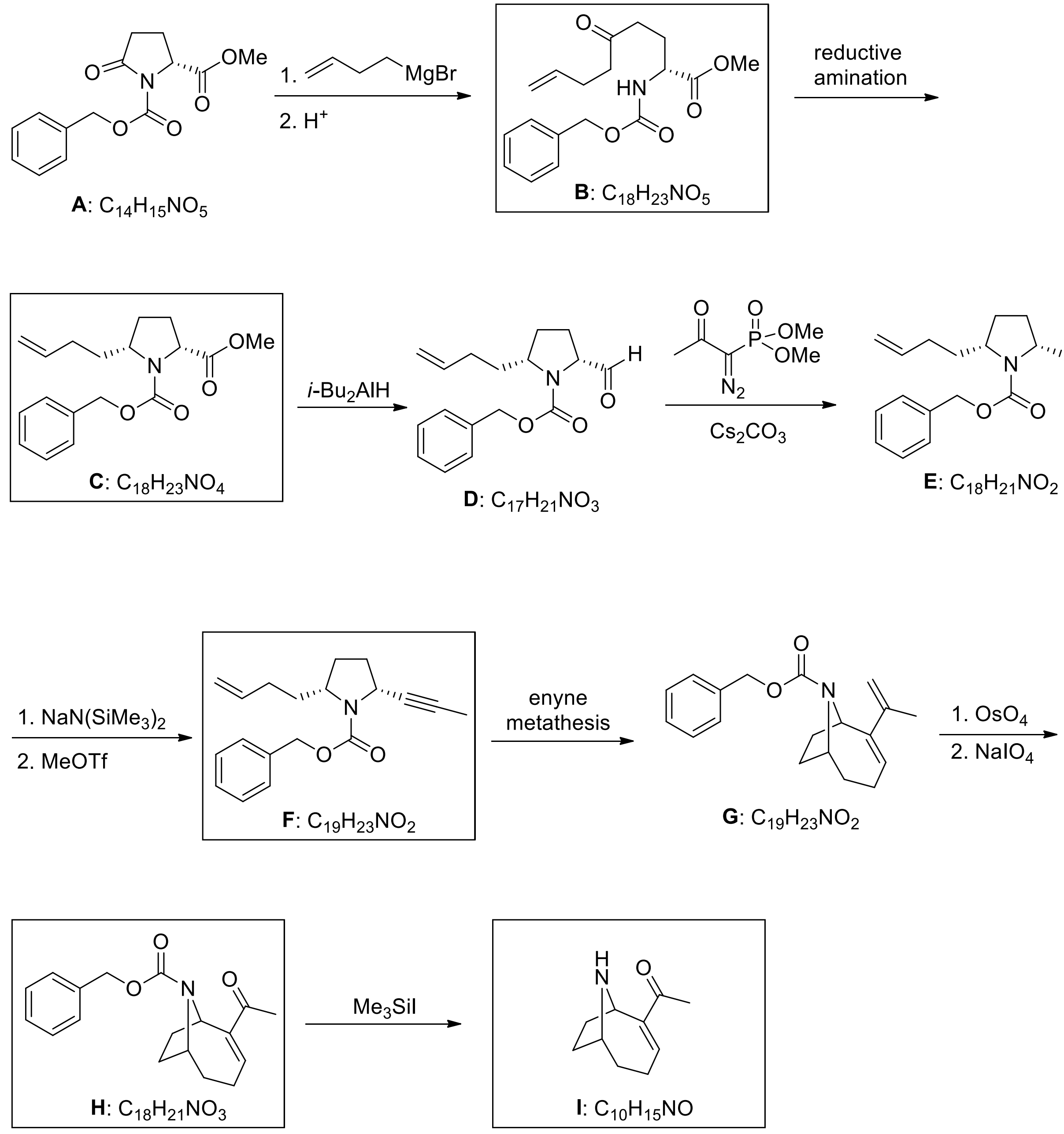
Task 28. Synthesis of Building Blocks for Fluorescent Markers

Compounds **A-I** are shown below:





Task 29. Synthesis towards Anatoxin-a



A: $C_{14}H_{15}NO_5$

B: $C_{18}H_{23}NO_5$

C: $C_{18}H_{23}NO_4$

D: $C_{17}H_{21}NO_3$

E: $C_{18}H_{21}NO_2$

F: $C_{19}H_{23}NO_2$

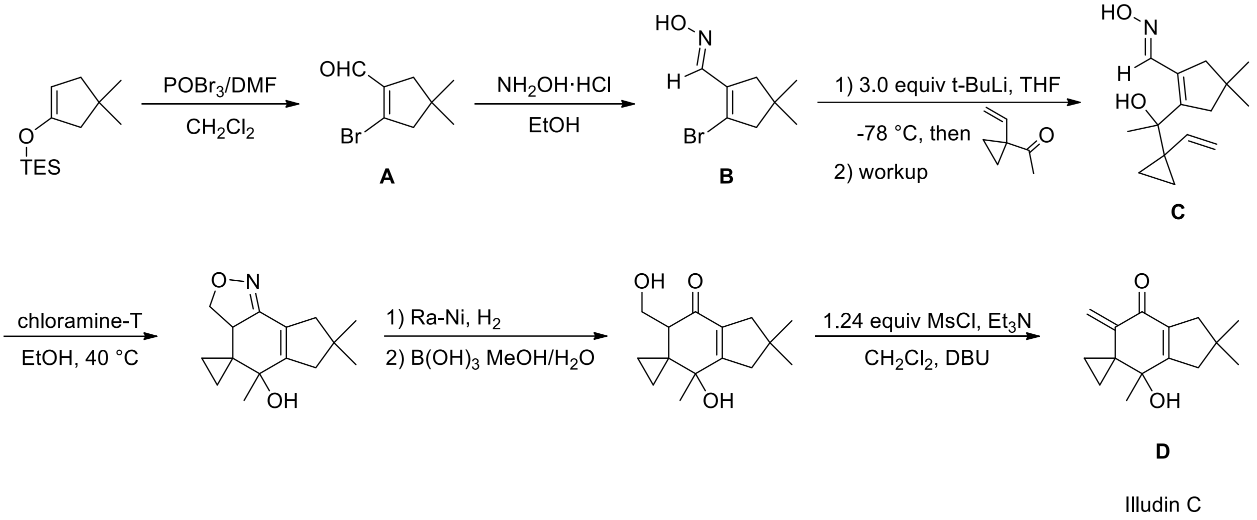
G: $C_{19}H_{23}NO_2$

H: $C_{18}H_{21}NO_3$

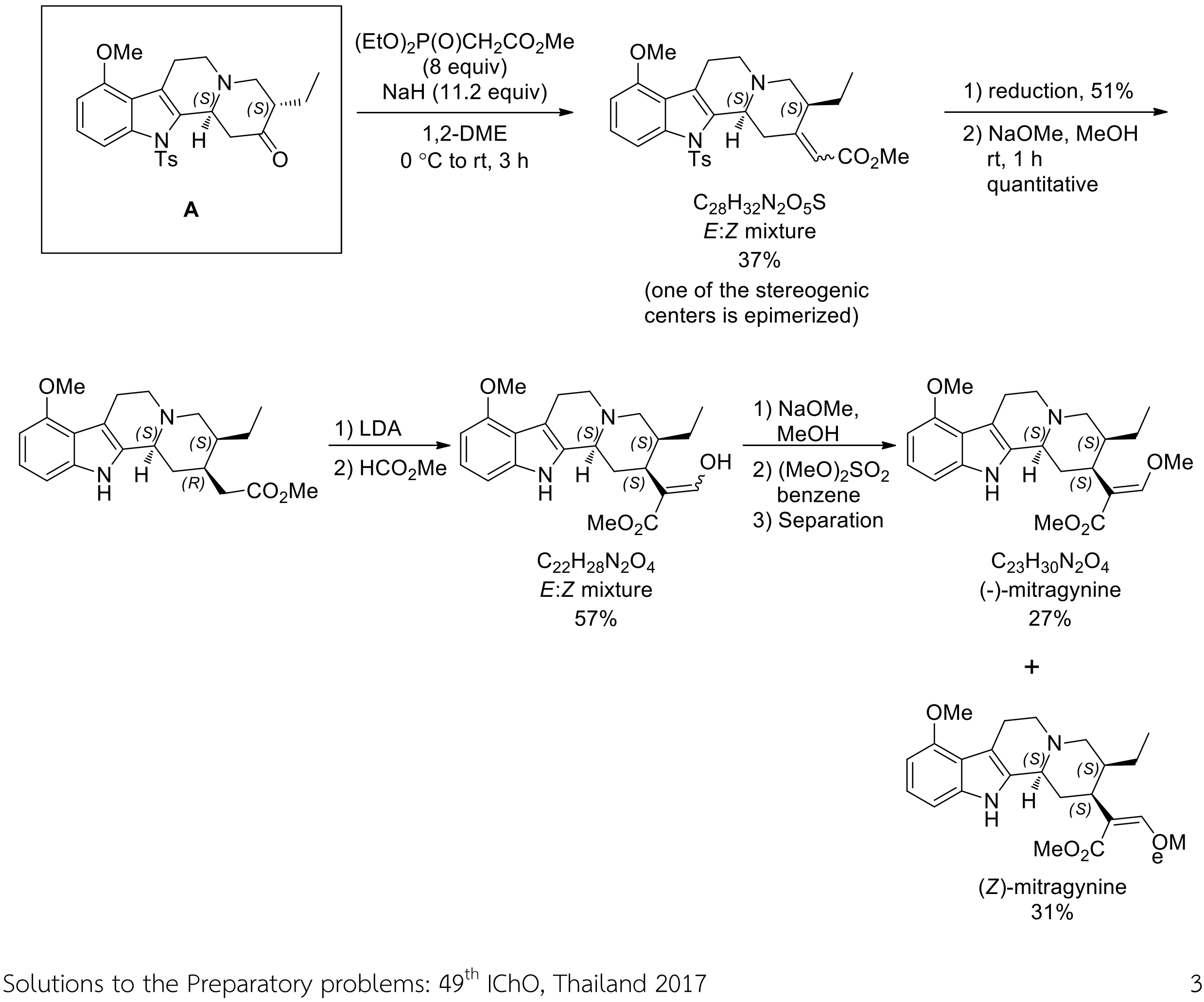
I: $C_{10}H_{15}NO$

Task 30. Total Synthesis of Illudin C

The structures of **A**, **B**, **C** and **D**:

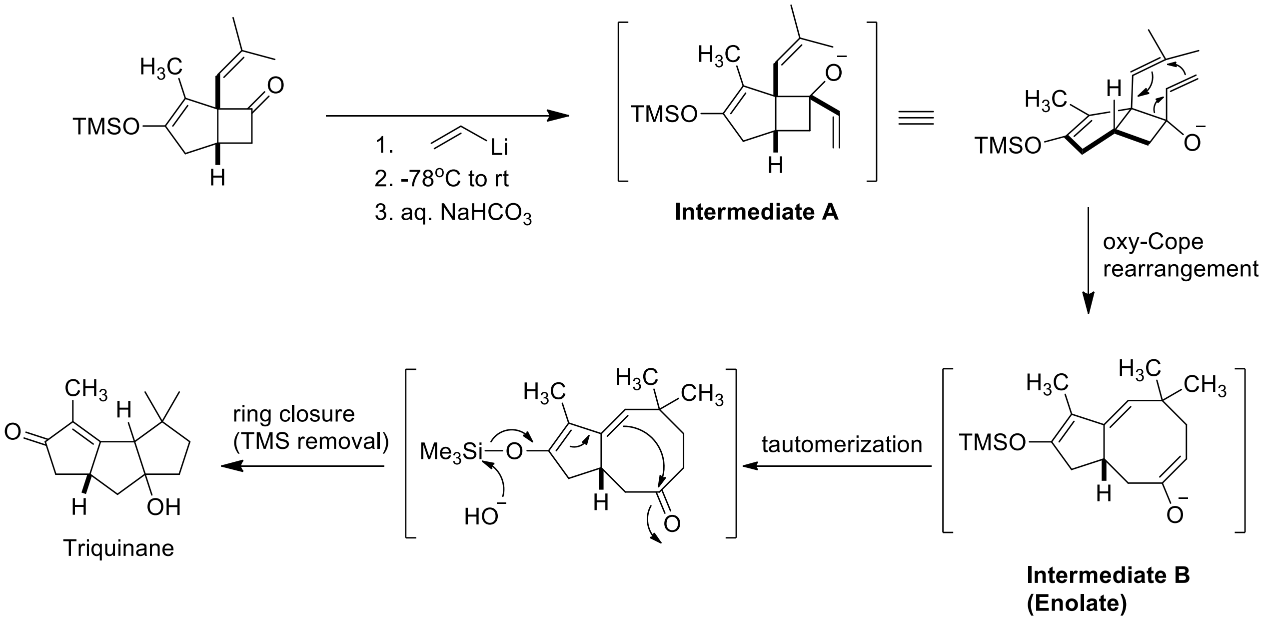


Task 31. Total Synthesis of μ-Opioid Receptor (MOR) Agonists



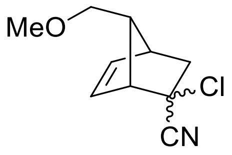
Task 32. Pericyclic Reaction

32.1)

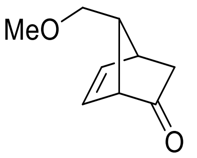


32.2)

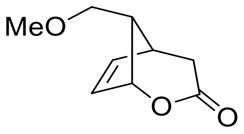
(i) Structures of compounds **C**-**G**



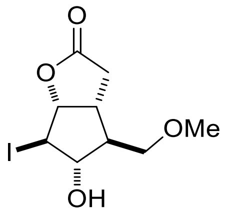
C



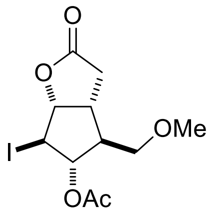
D



E

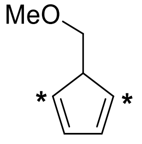


F

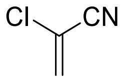


G

(ii)



1



2

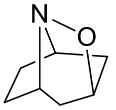
Either position on compound **1** is correct.

(iii) Two.

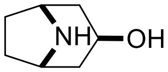
Reaction between **1** and **2** will give a pair of enantiomers which are inseparable. *(Note: the two enantiomers can be resolved but this process is not mentioned in the context.)* The subsequent processes, although generated a few new chiral centers, employed achiral reagent and the newly formed stereocenters were controlled by the existing stereochemistry. Therefore, stereochemical information was carried over from compound **C** to compound **3**.

32.3)

(i)

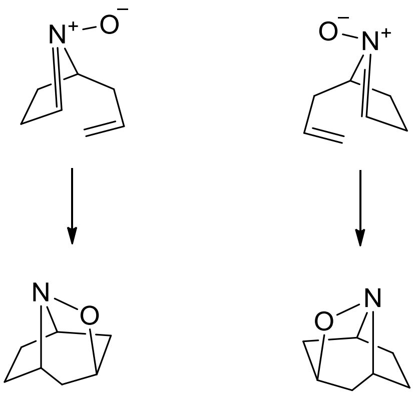


I



J

(ii) Racemic mixture of **H** will give product **I** which has a plane of symmetry. Therefore, reduction of **I** (only a stereoisomer) will give only 1 possible product **J**.



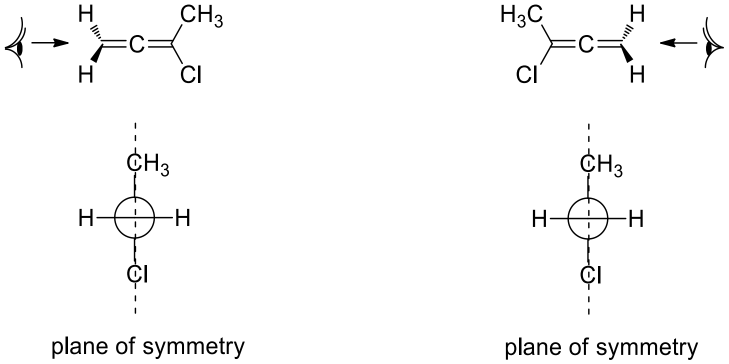
I **I'**

Note: *Compound I has a plane of symmetry, thus its mirror image (compound I') is identical (meso-compound).*

Task 33. Stereoisomers without Stereocenter

Hint: Student is encouraged to use chemistry model to figure out the plane of symmetry and the C_2–symmetry in each molecule.

33.1) (i) From the possible enantiomeric pair,

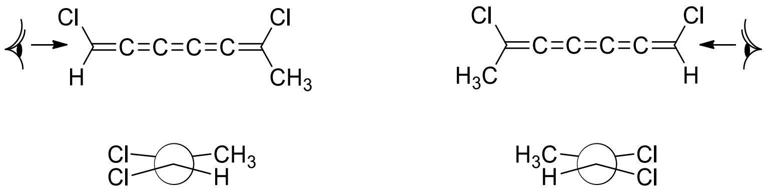


The molecule has a plane of symmetry, therefore, the structure is achiral.

(ii) From the possible enantiomeric pair,

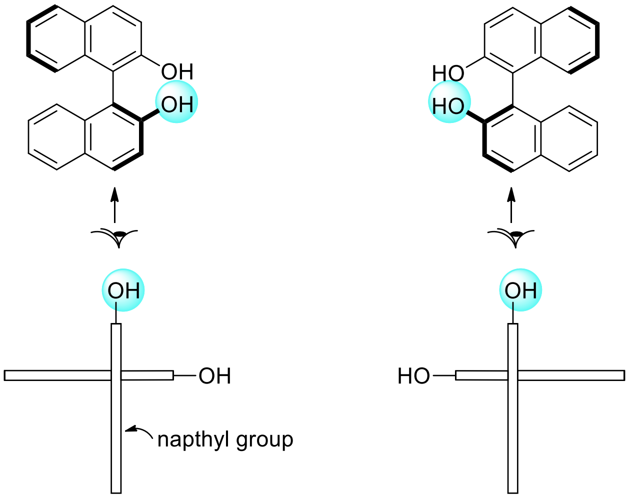
There is no plane of symmetry in these two molecules. Therefore, these two mirror image structures are non-superimposable. The structure is chiral.

(iii) From the structure of cumulene,



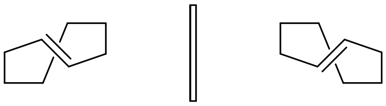
This molecule is flat. As a result, there is a plane of symmetry in this molecule. Consequently, its mirror image is achiral.

(iv) From the possible enantiomeric pair,

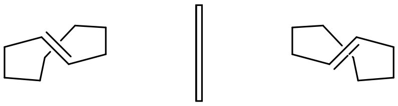


There is no plane of symmetry in these two molecules. Therefore, these two mirror image structures are non-superimposable. The structure is chiral.

33.2 (i)



trans-cyclooctene



trans-cyclononene

Enantiomers of *trans*-cyclooctene and *trans*-cyclononene are shown above. The two different structures are mirror images of each other and they are non-superimposable.

(ii) The enantiomers of both cycloalkanes are configurational isomers. The enantiomers can be interconverted *via* the ring flipping, similar to that of the chair cyclohexane. The *trans* double bond adds a considerable degree of rigidity to the ring. Since the *trans*-cyclononene has more carbon atoms so it is more flexible and can undergo the configuration inter-conversion more readily.