

Chemistry: The flavor of life

SOLUTIONS TO Preparatory Problems

46th International Chemistry Olympiad (IChO - 2014)

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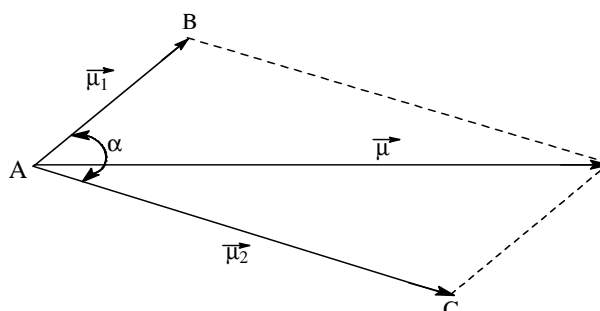
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PART I. THEORETICAL PROBLEMS

Problem 1. Polar and non-polar molecules

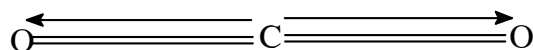
1. The net dipole moment μ is calculated as follows:



$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \alpha \quad (1)$$

2.

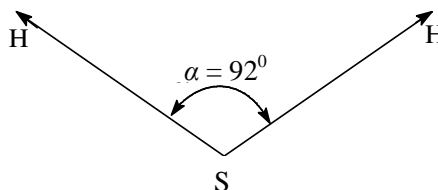
2.1 The geometry of CO_2 :



Because two bond moments of μ_{CO} have opposite directions and cancel each other out, the net dipole moment for CO_2 is zero. Therefore:

$$\mu_{\text{CO}_2} = 0$$

2.2 The geometry of H_2S :



From the general equation (1),



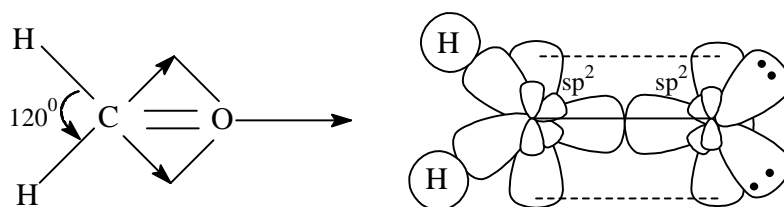
$$\mu_{\text{H}_2\text{S}}^2 = \mu_{\text{HS}}^2 + \mu_{\text{HS}}^2 + 2\mu_{\text{HS}}\mu_{\text{HS}}\cos\alpha = 2\mu_{\text{HS}}^2(1 + \cos\alpha) = 4\mu_{\text{HS}}^2\cos^2\frac{\alpha}{2}$$

$$\mu_{\text{H}_2\text{S}} = 2\mu_{\text{HS}}\cos\frac{\alpha}{2}$$

Therefore, $\mu_{\text{H}_2\text{S}} = 2 \times \frac{2.61 \times 10^{-30}}{3.33 \times 10^{-30}} \times \cos\frac{92}{2} = 1.09 \text{ D}$

3.

3.1



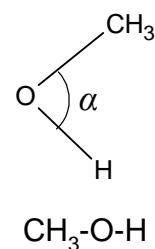
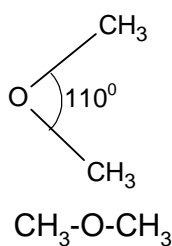
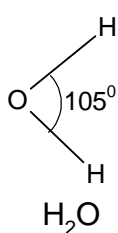
3.2 Since $\chi_{\text{C}} > \chi_{\text{H}}$, $\mu_{\text{C-H}}$ has the direction showed in the above plot, and

$$\mu_{\text{H-C-H}} = 2\mu_{\text{C-H}}\cos\frac{120}{2} = 2 \times 0.4 \times 0.5 = 0.4 \text{ D}$$

$\mu_{\text{C=O}}$ also has the direction toward the O atom. Therefore, the net dipole moment μ of the molecule is

$$\mu_{\text{HCH}} = \mu_{\text{HCH}} + \mu_{\text{C=O}} = 0.4 + 2.3 = 2.7 \text{ D}$$

4. We can plot the geometry of the three molecules involved in this problem in the following scheme:





- The dipole moment μ is a vector which can be calculated by adding individual bond moments μ_1 and μ_2

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \alpha \quad (1)$$

α is the angle formed by the individual bond moments.

- The dipole moment μ in the water molecule with the bond angle α formed by the two bond moments of O-H can be calculated as follows.

From equation (1) we have

$$\begin{aligned} \mu &= (2\mu_{\text{OH}}^2 + 2\mu_{\text{OH}}^2 \cos \alpha)^{1/2} \\ &= [2\mu_{\text{OH}}^2 (1 + \cos \alpha)]^{1/2} = \left[4\mu_{\text{OH}}^2 \cos^2 \frac{\alpha}{2} \right]^{1/2} \\ &= 2\mu_{\text{OH}} \cos \frac{\alpha}{2} \end{aligned}$$

Given $\alpha = 105^\circ$, the bond moment μ_{OH} in water can be calculated:

$$1.84 = 2\mu_{\text{OH}} \cos \frac{105}{2} \rightarrow \mu_{\text{OH}} = 1.51 \text{ D}$$

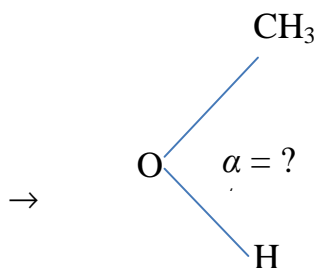
Similarly, we can calculate the bond moment for O-CH₃ in dimethylether:

$$1.29 = 2\mu_{\text{OCH}_3} \cos \frac{110}{2} \rightarrow \mu_{\text{OCH}_3} = 1.12 \text{ D}$$

- In methanol, the individual bond moments are given as $\mu_1 = \mu_{\text{OH}}$ and $\mu_2 = \mu_{\text{OCH}_3}$ as in water and dimethylether. The bond angle α is formed by the two individual bond moments.

From equation (1), $\cos \alpha$ is:

$$\begin{aligned} \cos \alpha &= \frac{(\mu^2 - \mu_1^2 - \mu_2^2)}{2\mu_1\mu_2} \\ &= \frac{(1.69^2 - 1.51^2 - 1.12^2)}{2 \times 1.51 \times 1.12} \\ \alpha &= 101^\circ 57' \end{aligned}$$



Therefore, the bond angle C – O – H in methanol is of $101^\circ 57'$



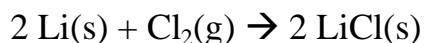
Problem 2. Calculations of lattice energy of ionic compounds

1.

1.1 Lithium reacts with water:



1.2 Lithium reacts with chlorine:

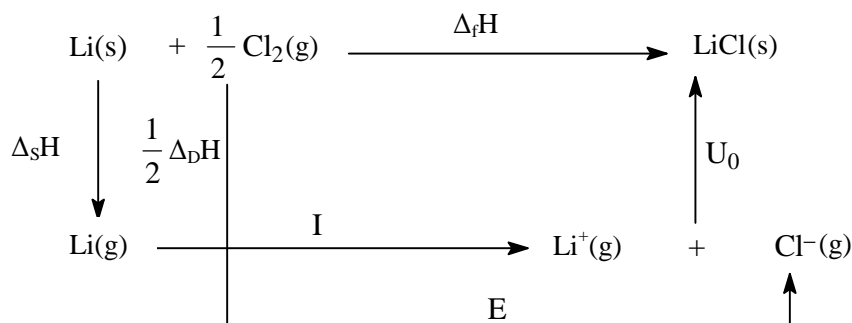


1.3 Lithium reacts with sulfuric acid:



2.

2.1 To calculate U_0 in accordance with Born-Haber cycle, the following cycle is constructed:



2.2 Based on this cycle and Hess's law, we have:

$$\Delta_f H = \Delta_s H + \frac{1}{2} \Delta_D H + I + E + U_0$$

$$\text{or } U_0 = \Delta_f H - \left(\Delta_s H + \frac{1}{2} \Delta_D H + I + E \right)$$

After converting all the numerical data to the same unit, we have:

$$U_0 = -402.3 - 159 - 121 - (5.40 - 3.84) \times 1.6 \times 10^{-19} \times 10^{-3} \times 6.022 \times 10^{23}$$

$$U_0 = -832.56 \text{ kJ/mol.}$$

$$3. U_0 = -287.2 \frac{Z_+ Z_- \sum v}{r_+ + r_-} \left(1 - \frac{0.345}{r_+ + r_-} \right)$$

For LiCl crystal, we have:

$$U_0 = -287.2 \frac{1 \times 1 \times 2}{0.62 + 1.83} \left(1 - \frac{0.345}{0.62 + 1.83} \right) = -201.43 \text{ kcal/mol}$$

To conveniently compare the results, we convert the obtained result to SI units:

$$U_0 = -201.43 \times 4.184 = -842.78 \text{ kJ/mol}$$

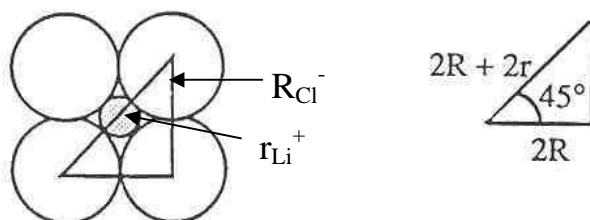
4.

According to the Born-Haber cycle and Kapustinskii empirical formula for lithium chloride crystal structure, both methods are close to the experimental value.

X

5.

5.1 The geometry diagram for octahedral holes is shown below.



where, R and r are the radii of Cl^- and Li^+ ions, respectively.

Based on the diagram, we have:

$$\cos 45^\circ = \frac{2R}{2R + 2r} = \frac{R}{R + r}$$

$$0.707 = \frac{R}{R + r} \rightarrow R = 0.707(R + r) \rightarrow r = 0.414 R$$

- The body edge length of the unit cell $\text{LiCl} = 2R + 2r = 5.14 \text{ \AA}$

$$2R + 2(0.414 R) = 5.14 \text{ \AA} \rightarrow R = 1.82 \text{ \AA} \text{ (radius of } \text{Cl}^- \text{)}$$



$$2(1.82 \text{ \AA}) + 2r = 5.14 \text{ \AA} \rightarrow r = 0.75 \text{ \AA} \text{ (radius of Li}^+\text{)}$$

5.2 Based on the experimental and theoretical data for the radii of Li⁺ and Cl⁻ ions, it is realized that:

♦ Both calculated radii of lithium and chloride ions are close to the experimental values. ☐

♦ Only the calculated radius of lithium ion is close to the experimental value. ☐

♦ Only the calculated radius of chloride ion is close to the experimental value. ☒

Problem 3. A frog in a well

1.

1.1 The general expression is given by:

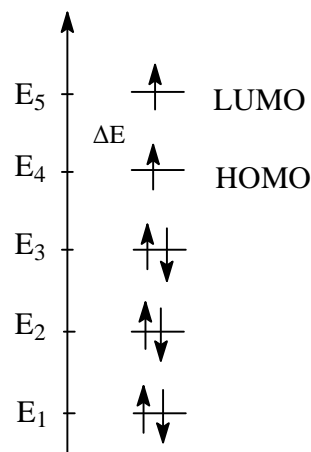
$$\Delta E_{\text{LUMO-HOMO}} = \frac{h^2}{8mL^2} \left[\left(\frac{N}{2} + 1 \right)^2 - \left(\frac{N}{2} \right)^2 \right] = \frac{h^2}{8mL^2} (N+1)$$

$$\Delta E_{\text{LUMO-HOMO}} = \frac{h^2}{8mL^2} (N+1) \quad (1)$$

1.2 From Planck's quantum theory:

$$\Delta E = \frac{hc}{\lambda} \quad (2) \quad \lambda \text{ can be given by:}$$

$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2} (N+1) \rightarrow \lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)} \quad (3)$$



2.

2.1

➤ For **BD**: $L = (2 \times 2 + 1)0.140 \text{ nm} = 5 \times 0.140 \times 10^{-9} \text{ m} = 7 \times 10^{-10} \text{ m} = 7.0 \text{ \AA}$

➤ For **HT**: $L = (2 \times 3 + 1)0.140 \text{ nm} = 7 \times 0.140 \times 10^{-9} \text{ m} = 9.8 \times 10^{-10} \text{ m} = 9.8 \text{ \AA}$



➤ For **OT**: $L = (2 \times 4 + 1)0.140 \text{ nm} = 9 \times 0.140 \times 10^{-9} \text{ m} = 12.6 \times 10^{-10} \text{ m} = 12.6 \text{ \AA}$

2.2 From the general equation (3), the wavelength λ for each of the dyes are given:

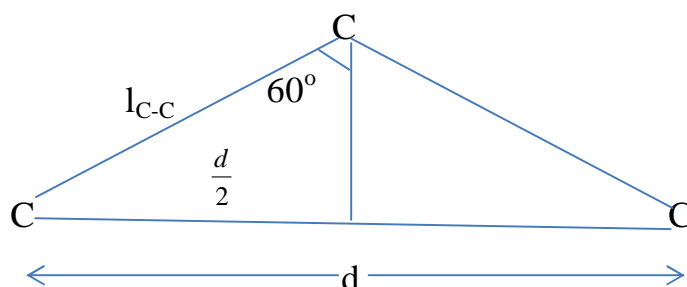
$$\lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)} = \frac{8(9.11 \times 10^{-31})(3 \times 10^8)}{6.626 \times 10^{-34}} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{L^2}{(N+1)}$$

$$\text{❖ BD: } \lambda = 3.30 \times 10^{12} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{(7 \times 10^{-10})^2}{(4+1)} = 3.234 \times 10^{-7} \text{ m} = 323.4 \text{ nm}$$

$$\text{❖ HT: } \lambda = 3.30 \times 10^{12} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{(9.8 \times 10^{-10})^2}{(6+1)} = 4.528 \times 10^{-7} \text{ m} = 452.7 \text{ nm}$$

$$\text{❖ OT: } \lambda = 3.30 \times 10^{12} \frac{L^2}{(N+1)} = 3.30 \times 10^{12} \frac{(12.6 \times 10^{-10})^2}{(8+1)} = 5.82 \times 10^{-7} \text{ m} = 582.0 \text{ nm}$$

3. The box length can be calculated based on the geometry of the C – C – C chain as follows:

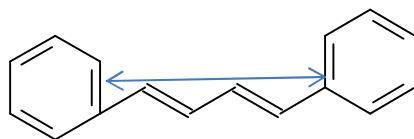


The box length is a combination of a number of the length of $\frac{d}{2}$ which is given by

$$\frac{d}{2} = l_{C-C} \times \sin 60 = (0.140 \times 10^{-9}) \times \sin 60 = 1.21 \times 10^{-10} \text{ m.}$$

Therefore, the box length for the three dye molecules can be calculated as follows:

For BD, the box length is consisted of 5 lengths of $\frac{d}{2}$:



❖ **BD:** $L = 1.21 \times 10^{-10} \text{ m} \times 5 = 6.05 \times 10^{-10} \text{ m} = 6.05 \text{ \AA}$

Similarly, the box length for **HT** has 7 lengths of $\frac{d}{2}$:

❖ **HT:** $L = 1.21 \times 10^{-10} \text{ m} \times 7 = 8.47 \times 10^{-10} \text{ m} = 8.47 \text{ \AA}$

The box length for **OT** has 9 lengths of $\frac{d}{2}$:

❖ **OT:** $L = 1.21 \times 10^{-10} \text{ m} \times 9 = 10.89 \times 10^{-10} \text{ m} = 10.89 \text{ \AA}$

4.

4.1 From equation (3), $\lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)}$, and therefore:

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}}$$

❖ For **BD:**

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}} = \sqrt{\frac{(328.5 \times 10^{-9})(6.626 \times 10^{-34})5}{8(9.11 \times 10^{-31})(3 \times 10^8)}} = 7.06 \times 10^{-10} = 7.06 \text{ \AA}$$

❖ For **HT:**

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}} = \sqrt{\frac{(350.95 \times 10^{-9})(6.626 \times 10^{-34})7}{8(9.11 \times 10^{-31})(3 \times 10^8)}} = 8.63 \times 10^{-10} = 8.63 \text{ \AA}$$

❖ For **OT:**

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8mc}} = \sqrt{\frac{(586.1 \times 10^{-9})(6.626 \times 10^{-34})9}{8(9.11 \times 10^{-31})(3 \times 10^8)}} = 12.64 \times 10^{-10} = 12.64 \text{ \AA}$$

4.2 The following table shows the values of the box length for the



investigated dyes calculated with different methods.

Substance	$L=(2k+1)0.140$ nm (1)	L calculated based on the bent chain (2)	L calculated from $\lambda_{\text{exp.}}$ (3)	Experimental L
BD	7.0	6.05	7.06	7.66
HT	9.8	8.47	8.63	8.64
OT	12.6	10.89	12.64	-

- Method (1) is the best fit ☐
- Method (2) is the best fit ☐
- Method (3) is the best fit ☒
- All methods (1), (2) , (3) are best fit ☐

Problem 4. Electron in a 2 or 3 – Dimensional Box

1.

$$\underline{1.1} \quad \Delta E = n^2 \frac{h^2}{8mL^2} - 1^2 \frac{h^2}{8mL^2} = \frac{h^2}{8mL^2} (n^2 - 1^2)$$

1.2 According to Planck's equation:

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m/s})}{1.374 \times 10^{-5} \text{ m}} = 1.446 \times 10^{-20} \text{ J}$$



$$\text{So } \Delta E = 1.446 \times 10^{-20} \text{ J} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg})(10.0 \times 10^{-9} \text{ m})^2} (n^2 - 1)$$

$$1.446 \times 10^{-20} \text{ J} = 6.025 \times 10^{-22} (n^2 - 1)$$

$$\rightarrow n^2 - 1 = 24.00 \rightarrow n^2 = 25.00 \rightarrow n = 5.00$$

$$\mathbf{n = 5}$$

2.

2.1 The quantum numbers are:

$$\text{Ground state (E}_{11}\text{)} \rightarrow n_x = 1, n_y = 1$$

$$\text{First excited state (E}_{21}\text{)} \rightarrow n_x = 2, n_y = 1$$

$$\text{Second excited state (E}_{12}\text{)} \rightarrow n_x = 1, n_y = 2$$

Since the energy levels, E_{xy} , are inversely proportional to L^2 , then the $n_x = 2, n_y = 1$ energy level will be lower than the $n_x = 1, n_y = 2$ energy level since $L_x > L_y$.

The first three energy levels, E_{xy} , in order of increasing energy are: $E_{11} < E_{21} < E_{12}$

2.2 Calculate the wavelength of light necessary to promote an electron from the first excited state to the second excited state.

$$E_{21} \rightarrow E_{12} \text{ is transition. } E_{xy} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

$$E_{12} = \frac{h^2}{8m} \left(\frac{1^2}{(8.00 \times 10^{-9} \text{ m})^2} + \frac{2^2}{(5.00 \times 10^{-9} \text{ m})^2} \right) = \frac{1.76 \times 10^{17} \text{ h}^2}{8m}$$

$$E_{21} = \frac{h^2}{8m} \left(\frac{2^2}{(8.00 \times 10^{-9} \text{ m})^2} + \frac{1^2}{(5.00 \times 10^{-9} \text{ m})^2} \right) = \frac{1.03 \times 10^{17} \text{ h}^2}{8m}$$

$$\Delta E = E_{12} - E_{21} = \frac{1.76 \times 10^{17} \text{ h}^2}{8m} - \frac{1.03 \times 10^{17} \text{ h}^2}{8m} = \frac{7.3 \times 10^{16} \text{ h}^2}{8m}$$

$$\Delta E = \frac{(7.3 \times 10^{16} \text{ m}^{-2})(6.626 \times 10^{-34} \text{ Js})^2}{8(9.11 \times 10^{-31} \text{ kg})} = 4.4 \times 10^{-21} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \text{ m/s})}{4.4 \times 10^{-21} \text{ J}} = 4.5 \times 10^{-5} \text{ m}$$



3.

$$\underline{3.1} \quad E = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = \frac{n^2 h^2}{8mL^2} = 6.173 \times 10^{-21} \text{ J}$$
$$n^2 = \frac{8mL^2}{h^2} E$$

If $L^3 = 8.00 \text{ m}^3$, then $L^2 = 4.00 \text{ m}^2$

$$\frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34})^2}{8 \left(\frac{0.032}{6.022 \times 10^{23}} \right)^4} = 2.582 \times 10^{-43} \text{ J}$$
$$n^2 = \frac{6.173 \times 10^{-21}}{2.582 \times 10^{-43}} = 2.39 \times 10^{22}; \quad n = 1.55 \times 10^{11}$$

$$\underline{3.2} \quad \Delta E = E_{n+1} - E_n = E_{1.55 \times 10^{11} + 1} - E_{1.55 \times 10^{11}}$$

$$\Delta E = (2n+1) \frac{h^2}{8mL^2} = [2(1.55 \times 10^{11}) + 1] \frac{h^2}{8mL^2} = 8.00 \times 10^{-31} \text{ J}$$

4. The energy levels are

$$E_{n_1, n_2, n_3} = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = E_1(n_1^2 + n_2^2 + n_3^2)$$

where E_1 combines all constants besides quantum numbers. The minimum value for all quantum numbers is 1, so the lowest energy is

$$E_{1,1,1} = 3E_1$$

The question asks about an energy 21/3 times this amount, namely $21E_1$. This energy level can be obtained by any combination of allowed quantum numbers such that

$$(n_1^2 + n_2^2 + n_3^2) = 21 = 4^2 + 2^2 + 1^2$$

The degeneracy, then is 6, corresponding to $(n_1, n_2, n_3) = (1, 2, 4), (1, 4, 2), (2, 1, 4), (2, 4, 1), (4, 1, 2),$ or $(4, 2, 1)$.



Problem 5. Tug of war

$$1. \Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^{\circ} + RT \ln \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}}$$

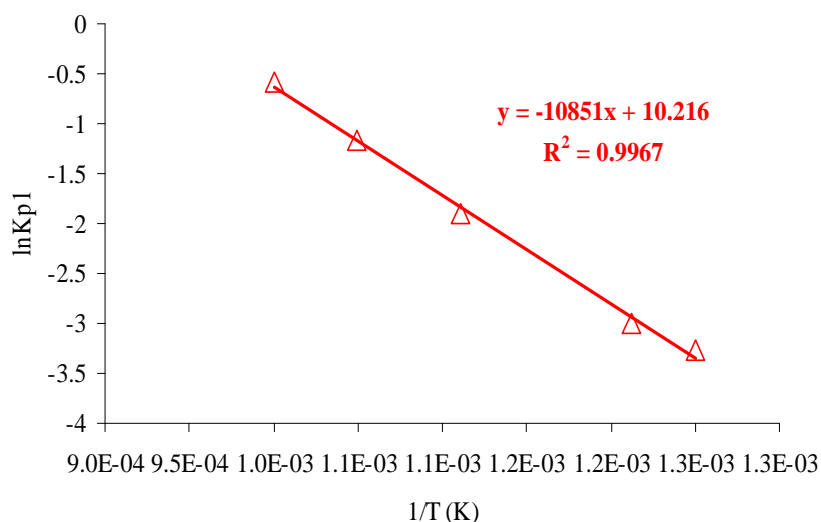
$$\text{At equilibrium: } \Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^{\circ} + RT \ln \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = 0$$

$$\Delta_r G^{\circ} = - RT \ln \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = - RT \ln K_{\text{p1}}$$

$$T / \text{K} = T / ^{\circ}\text{C} + 273;$$

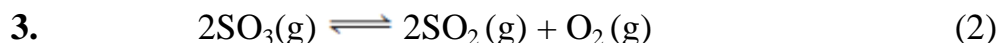
T / K	800	825	900	953	100
$\ln K_{\text{p1}}$	-3.263	-3.007	- 1.899	-1.173	-0.591

2. Plot $\ln K_{\text{p1}}$ against $1/T$:





Assuming that $\Delta_r H^\circ$ is temperature independent, the slope of this plot is $-\Delta_r H^\circ/R$, so that $\Delta_{rxn} H^\circ = 90.2 \text{ kJ/mol}$.

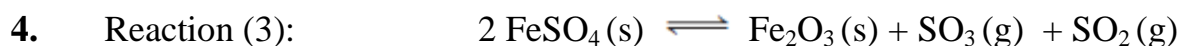


A best-fit equation is $\ln K_{p1} = -10851(1/T) + 10.216$ with R-squared value of 0.9967. We can use this equation to estimate the K_{p1} at $(651.33 + 273) = 924.33 \text{ K}$ because $\Delta_{rxn} H^\circ$ is temperature independent.

$$\ln K_{p1} = -10851(1/924.33) + 10.216 \rightarrow \ln K_{p1} = -1.523313881 \rightarrow K_{p1} = 0.218$$

For reaction (2), the equilibrium constant is expressed as:

$$K_{p2} = \frac{P_{\text{SO}_2}^2 P_{\text{O}_2}}{P_{\text{SO}_3}^2} = (K_{p1})^2 = (0.218)^2 = 0.047524$$



Decomposition:

-

-

-

Equilibrium:

P-a

P+a

Reaction (4):



Initial P:

P

P

0

Change

-a

+a

+a/2

Equilibrium

P-a

P+a

a/2

At equilibrium: partial pressure of oxygen = $21.28/760 = 0.028 \text{ atm}$

$$a/2 = 0.028 \text{ atm} \rightarrow a = 0.056 \text{ atm}$$

Equilibrium constant for (4):

$$K_{p4} = \frac{P_{\text{SO}_2}^2 P_{\text{O}_2}}{P_{\text{SO}_3}^2} = (K_{p1})^2 = (0.218)^2 = 0.047524$$

$$K_{p4} = \frac{P_{\text{SO}_2}^2 P_{\text{O}_2}}{P_{\text{SO}_3}^2} = \frac{(P+a)^2 (a/2)}{(P-a)^2} = \frac{(P+0.056)^2 0.028}{(P-0.056)^2} = 0.047524$$



$$\frac{(P + 0.056)^2 \cdot 0.028}{(P - 0.056)^2} = 0.047524$$

$$\rightarrow \frac{(P + 0.056)^2}{(P - 0.056)^2} = 1.6973$$

$$\rightarrow \frac{(P + 0.056)}{(P - 0.056)} = 1.303 \quad \rightarrow P + 0.056 = 1.303P - 0.073$$

$$\rightarrow 0.303P = 0.12896 \quad \rightarrow P = 0.425 \text{ atm}$$

Equilibrium constant for (3) $2 \text{FeSO}_4(\text{s}) \rightleftharpoons \text{Fe}_2\text{O}_3(\text{s}) + \text{SO}_3(\text{g}) + \text{SO}_2(\text{g})$

$$K_{p3} = P_{\text{SO}_3} P_{\text{SO}_2} = (P-a)(P+a) = (0.425 - 0.056)(0.425 + 0.056) = 0.177$$

5. Calculate the percent of FeSO_4 decomposed?

Mole number of $\text{SO}_3 = \text{SO}_2$ comes from the decomposition of FeSO_4 :

$$PV = nRT, n = PV/PT = (0.425)1 / (0.082 \times 924.33) = 5.6 \times 10^{-3} \text{ moles}$$

$$\text{Molar number of } \text{FeSO}_4 \text{ decomposed} = 2n_{\text{SO}_3} = 0.0112 \text{ mol}$$

$$\text{Mass of } \text{FeSO}_4 \text{ decomposed} = 0.0112 \times 151.91 = 1.70 \text{ grams}$$

$$\text{Percent of } \text{FeSO}_4 \text{ decomposed} = 1.70/15.19 = 11.21 \text{ \%}.$$

Problem 6. Radiochemistry

1.

²⁰⁴ Pb	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb
x			

2. Assume that the mineral initially contained $n_{1,0}$ moles of ^{238}U , $n_{2,0}$ moles of ^{206}Pb , and n_3 moles of ^{204}Pb ; and at present, it contains n_1 moles of ^{238}U , n_2 moles



of ^{206}Pb , and n_3 moles of ^{204}Pb (this isotope is not generated by the decay of ^{238}U and ^{235}U). The age of the zircon mineral is usually very large, and we can consider that the century equilibrium for the decay process has been reached (i.e. loss of 1 mole of ^{238}U will lead to formation of 1 mole of ^{206}Pb). By conservation of mass, we have the following equation:

$$n_1 + n_2 = n_{1,0} + n_{2,0} \quad (1)$$

Dividing (1) by n_3 :

$$\begin{aligned} n_1/n_3 + n_2/n_3 &= n_{1,0}/n_3 + n_{2,0}/n_3 \\ \rightarrow n_2/n_3 &= n_{1,0}/n_3 - n_1/n_3 + n_{2,0}/n_3 \end{aligned} \quad (2)$$

In addition, we have $n_{1,0} = n_1 e^{\lambda t}$, where λ is the decay constant of ^{238}U , and t is the age of the mineral,

$$\rightarrow n_2/n_3 = n_1 e^{\lambda t}/n_3 - n_1/n_3 + n_{2,0}/n_3 = (n_1/n_3)(e^{\lambda t} - 1) + n_{2,0}/n_3 \quad (3)$$

$$\rightarrow e^{\lambda t} - 1 = \frac{n_2/n_3 - n_{2,0}/n_3}{n_1/n_3}$$

$$\rightarrow e^{\lambda t} = 1 + \frac{n_2/n_3 - n_{2,0}/n_3}{n_1/n_3}$$

$$\rightarrow t = \frac{1}{\lambda} \ln\left(1 + \frac{n_2/n_3 - n_{2,0}/n_3}{n_1/n_3}\right) \quad (4)$$

According to the data given:

$$\frac{n_2}{n_3} = \frac{\frac{14.30}{206}}{\frac{0.277}{204}} = 51.12; \quad \frac{n_{2,0}}{n_3} = \frac{\frac{24.10}{206}}{\frac{1.4}{204}} = 17.05$$

$$\frac{n_1}{n_3} = \frac{\frac{99.275}{238}}{\frac{0.277}{204}} = 307.19$$

$$t = \frac{4.47 \times 10^9}{0.693} \ln\left(1 + \frac{51.12 - 17.05}{307.19}\right) = 6.78 \times 10^8 \text{ years}$$



$$m_0(^{235}\text{U}) = 0.721 \times e^{\frac{0.693}{7.038 \times 10^8} \times 6.78 \times 10^8} = 1.406 \text{ g}$$

$$m_0(^{238}\text{U}) = 99.275 \times e^{\frac{0.693}{4.47 \times 10^8} \times 6.78 \times 10^8} = 110.28 \text{ g}$$

$$m_0(^{235}\text{U}) / m_0(^{238}\text{U}) = 1.406 / 110.28 = 0.0127$$

3. After 99% of Fe^{3+} precipitated, the concentration of the remaining Fe^{3+} in the solution is:

$$[\text{Fe}^{3+}] = 2 \times 0.05 \times 10^{-2} = 1 \times 10^{-3} \text{ M}$$

The concentration of hydroxide ions necessary to maintain a Fe^{3+} concentration of 10^{-3} M in the solution is:

$$[\text{OH}^-] = \left(\frac{T_{\text{Fe}(\text{OH})_3}}{Fe^{3+}} \right)^{\frac{1}{3}} = \left(\frac{3.8 \times 10^{-38}}{10^{-3}} \right)^{\frac{1}{3}} = (38)^{\frac{1}{3}} \times 10^{-12} \text{ M}$$

Thus, the pH value of the solution can be calculated as follows:

$$\text{pH} = -\log \{ 10^{-14} / [(38)^{1/3} \times 10^{-12}] \} = 2 + (1/3)\log 38 = 2.53$$

At this pH, the reaction quotient of the dissociation of $\text{UO}_2(\text{OH})_2$ in 0.01 M of solution is:

$$[\text{UO}_2^{2+}][\text{OH}^-]^2 = 0.01 \times [(38)^{1/3} \times 10^{-12}]^2 = 1.13 \times 10^{-25} < 10^{-22}$$

Since the ionic product is much smaller than the solubility product of $\text{UO}_2(\text{OH})_2$, we can conclude that uranium cannot precipitate under these conditions.

4. Volume ratio of the two phases: $V_{\text{aq}}/V_{\text{org}} = 1000 : 500 = 2$

Let x represent the equilibrium concentration of $\text{UO}_2(\text{NO}_3)_2$ in the aqueous phase.

Let C_0 represent the initial concentration of $\text{UO}_2(\text{NO}_3)_2$ in the organic phase.



The equilibrium concentration of $\text{UO}_2(\text{NO}_3)_2$ in the organic phase is calculated as follows:

$$C_{\text{org}} = (V_{\text{aq}}/V_{\text{org}})(C_0 - x)$$

$$D = \frac{C_{\text{org}}}{x} = \frac{2(C_0 - x)}{x} = 10 \quad (6)$$

$$x : C_0 = 1 : 6 = 16.67\%.$$

5. 500 mL of organic solvent may be divided into n equal portions for extraction.

Volume ratio of the two phases: $V_{\text{aq}}/V_{\text{org}} = 1000 : (500/n) = 2n$

- After the first extraction:

$$D = \frac{C_{\text{org}}}{x_1} = \frac{2n(C_0 - x_1)}{x_1} = 10 \quad (7)$$

$$\rightarrow x_1 = \frac{2nC_0}{D + 2n} \quad (8)$$

- For the second extraction, the initial concentration of the aqueous phase is x_1 , while the equilibrium concentration is x_2 . Using equation (8), we replace x_2 with x_1 , and x_1 with C_0 to obtain the following expression:

$$x_2 = \frac{2nx_1}{D + 2n} = \left(\frac{2n}{D + 2n} \right)^2 C_0 \quad (9)$$

- After n extractions, the concentration of $\text{UO}_2(\text{NO}_3)_2$ remaining in the aqueous phase is:

$$x_n = \left(\frac{2n}{D + 2n} \right)^n C_0 \quad (10)$$

% $\text{UO}_2(\text{NO}_3)_2$ remaining in the aqueous phase after n extractions is:

$$\frac{x_n}{C_0} 100\% = \left(\frac{2n}{D + 2n} \right)^n 100\%$$



n =	1	2	3	4	5	6
$\left(\frac{2n}{D+2n}\right)^n 100\% =$	16.67	8.16	5.27	3.9	3.1	2.63

$$n = 5 \rightarrow \frac{x_n}{C_0} 100\% = \left(\frac{2n}{D+2n}\right)^n < 4\%$$

Thus, the optimal approach is to divide 500 mL of solvent into 5 portions and extract 5 times.

Other schemes are acceptable, if all calculations and justifications are reasonable.

Problem 7. Applied thermodynamics

1.

1.1 Based on the above data:

$$\Delta G^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T$$

Reaction (1): $\Delta G^\circ_T(1) = (-112298.8 + 5.94T) - T(54.0 + 6.21\ln T)$

$$\Delta G^\circ_T(1) = -112298.8 - 48.06T - 6.21T\ln T$$

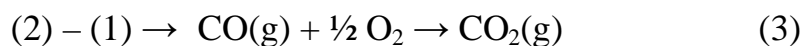
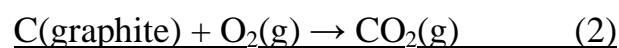
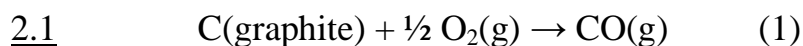
$\Delta G^\circ_T(1)$ decreases with an increase in temperature.

Reaction (2): $\Delta G^\circ_T(2) = (-393740.1 + 0.77T) - T(1.54 - 0.77\ln T)$

$$\Delta G^\circ_T(2) = -393740.1 - 0.77T + 0.77T\ln T$$

1.2 $\Delta G^\circ_T(2)$ increases with an increase in temperature.

2.



We have, $\Delta G^\circ_T(3) = \Delta G^\circ_T(2) - \Delta G^\circ_T(1)$



2.2 Substitute the values in:

$$\Delta G^\circ_T(3) = (-393740.1 - 0.77T + 0.77T \ln T) - (-112298.8 - 48.06T - 6.21T \ln T)$$

$$\Delta G^\circ_T(3) = -281441.3 + 47.29T - 6.98T \ln T$$

$$\text{At } 1673 \text{ K: } \Delta G^\circ_T(3) = -115650 \text{ J/mol}$$

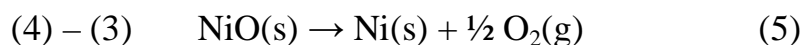
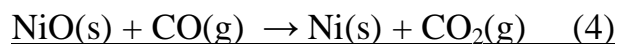
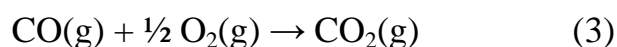
2.3 Since $\Delta G^\circ = -RT \ln K_p$, the equilibrium constant K_p for reaction (3) can be calculated as follows:

$$\ln K_{p,1673}(3) = -\frac{\Delta G^\circ_{1673}(3)}{RT} = \frac{115650}{8.314 \times 1673} = 8.313457$$

$$\rightarrow K_{p,1673}(3) = 4083$$

3.

3.1



3.2

At 1673 K, we have:

$$\text{For reaction (4): } K_p(4) = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{99}{1}$$

$$\text{For reaction (3): } K_p(3) = \frac{p_{\text{CO}_2}}{p_{\text{CO}} p_{\text{O}_2}^{1/2}} = 4083 \quad \text{or} \quad p_{\text{O}_2}^{1/2} = \frac{p_{\text{CO}_2}}{p_{\text{CO}} 4083} = \frac{K_p(4)}{4083} = \frac{99}{4083}$$

$$\text{For reaction (5): } K_p(5) = p_{\text{O}_2}^{1/2} = \frac{p_{\text{CO}_2}}{p_{\text{CO}} K_p(3)} = \frac{K_p(4)}{K_p(3)} \quad \text{or}$$

$$K_p(5) = p_{\text{O}_2}^{1/2} = \frac{K_p(4)}{K_p(3)} = \frac{99}{4083} = 0.024247 = 2.4247 \times 10^{-2}$$

$$\text{Hence, } p_{\text{O}_2} = [K_p(5)]^2 = (2.4247 \times 10^{-2})^2 \quad \text{and} \quad p_{\text{O}_2} = 5.88 \times 10^{-4} \text{ bar} = 58.8 \text{ Pa}$$

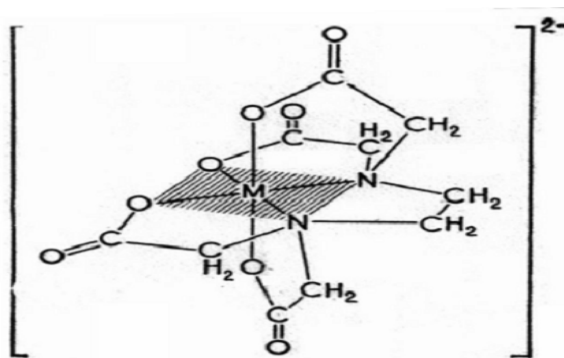


Problem 8. Complex compound

1. How many atoms of EDTA are capable of binding with the metal ions upon complexation?

- 1.1 ☐ ☐ ☒ ☐
 2 4 6 8

1.2



2.

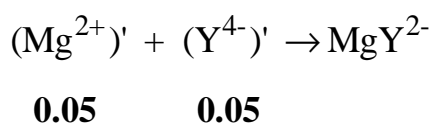
2.1 Let $[H^+]$ be h and at $pH = 10.26$:

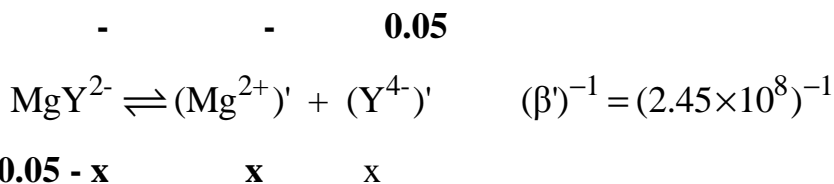
$$\beta' = \beta \alpha_{Mg^{2+}} \alpha_{Y^{4-}}$$

$$= \beta \frac{1}{1 + \beta h^{-1}} \frac{K_{a4}}{h + K_{a4}} = 10^{8.69} \frac{1}{1 + 1.58 \times 10^{-13} \times 10^{10.26}} \frac{10^{-10.26}}{10^{-10.26} + 10^{-10.26}}$$

$$\beta' = \beta \alpha_{Mg^{2+}} \alpha_{Y^{4-}} = 10^{8.69} \times 1 \times 0.5 = 2.45 \times 10^8$$

2.2 At $pH = 10.26$:





$$C_{Mg^{2+}} = C'_{Mg^{2+}} = x = 1.43 \times 10^{-5} (M)$$

$$C_{\text{Mg}^{2+}} [\text{OH}^-]^2 = 1.43 \times 10^{-5} (10^{-3.74})^2 = 10^{-12.32} < K_{\text{s}(\text{Mg}(\text{OH})_2)} = 10^{-10.95}$$

Hence no $\text{Mg}(\text{OH})_2$ precipitate appears

Precipitation

X

No precipitation

3.

3.1

$$[\text{CN}^-] = C_{\text{CN}^-} \frac{K_a}{h + K_a} = \frac{1.400 \times 1000}{65 \times 20.00} \frac{10^{-9.35}}{10^{-10.50} + 10^{-9.35}} = 1.00 \text{ (M)}$$

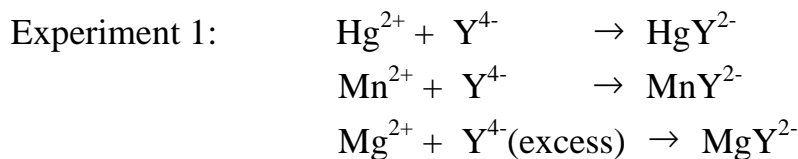
$$\alpha_{\text{Hg}^{2+}} = \frac{1}{1 + \beta_{\text{Hg}(\text{CN})_4^{2-}} [\text{CN}^-]^4} = \frac{1}{1 + 10^{38.97} \times 1^4} = 1.00 \times 10^{-38.97}$$

$$\alpha_{Y^{4-}} \approx \frac{K_{a4}}{h + K_{a4}} = \frac{10^{-10.26}}{10^{-10.50} + 10^{-10.26}} = 0.635$$

$$\beta'_{\text{HgY}^{2-}} = \beta_{\text{HgY}^{2-}} \alpha_{\text{Hg}^{2+}} \alpha_{\text{Y}^{4-}} = 10^{21.80} (1.00 \times 10^{-38.97}) 0.635 = 4.29 \times 10^{-18}$$

$\beta'_{\text{HgY}^{2-}}$ is very small, Hg^{2+} is cannot be titrated in the experiment 2.

3.2 Chemical equations:

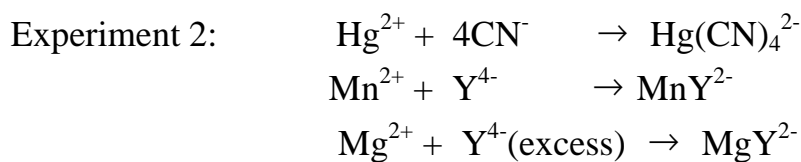


$$(C_{Mn^{2+}} + C_{Hg^{2+}}) \times 20.00 = 25.00 \times 0.040 - 12.00 \times 0.025 \quad (1)$$



46th International Chemistry Olympiad
Hanoi, Vietnam – 2014

Preparatory Problem
Solutions



$$C_{\text{Mn}^{2+}} \times 20.00 = 25.00 \times 0.040 - 20.00 \times 0.025 \quad (2)$$

According to (1) and (2): $C_{\text{Mn}^{2+}} = 0.025 \text{ M}$; $C_{\text{Hg}^{2+}} = 0.010 \text{ M}$

4.

4.1 As $K_{a3}/K_{a4} > 1 \times 10^4$ and $K_{a4} < 10^{-9}$ only one endpoint can be determined for the titration of H_2Y^{2-} :



4.2 $\text{pH}_{\text{EP}} = \text{pH}(\text{HY}^{3-}) = (\text{p}K_{a3} + \text{p}K_{a4})/2 = 8.21$

4.3 $\text{pH}_{\text{EP}} = \text{pH}_{(\text{phenol red})}$, hence the most suitable indicator is phenol red



Bromothymol blue

Phenol red

Phenolphthalein

4.4

If the final pH is 7.60 the percentage of H_2Y^{2-} that is titrated:

$$\frac{[\text{HY}^{3-}]}{[\text{H}_2\text{Y}^{2-}] + [\text{HY}^{3-}]} = \frac{K_{a3}}{[\text{H}^+] + K_{a3}} 100 = \frac{10^{-6.16}}{10^{-6.16} + 10^{-7.60}} 100 = 96.5\%$$

The volume of NaOH solution needed to reach pH of 7.60 is:

$$V_{\text{NaOH}} = V_1 = (0.25 \times 10 \times 0.965)/0.2 = 12.06 \text{ (mL)}$$

$$V_{\text{EP}} = V_2 = (0.25 \times 10)/0.20 = 12.50 \text{ (mL)}$$

$$q = \frac{12.06 - 12.50}{12.50} \times 100\% \approx -3.5\%$$

(As 96.5% of H_2Y^{2-} is titrated, 3.5% of the analyte has not been titrated, or the error $q = -3.5\%$.)



Problem 9. Lead compounds

1.

☐

(I)

☐

(II)

☐

(III)

☒

(IV)

2.

☒

(I)

☐

(II)

☐

(III)

☐

Other

3.

3.1 Condition for precipitation of:

$$\text{PbSO}_4 : C_{\text{Pb}^{2+}(1)} \geq \frac{10^{-7.66}}{0.02} = 1.09 \times 10^{-6} \text{ (M)}$$

$$\text{PbC}_2\text{O}_4 : C_{\text{Pb}^{2+}(2)} \geq \frac{10^{-10.05}}{5.0 \times 10^{-3}} = 1.78 \times 10^{-8} \text{ (M)}$$

$$\text{PbI}_2 : C_{\text{Pb}^{2+}(3)} \geq \frac{10^{-7.86}}{(9.7 \times 10^{-3})^2} = 1.47 \times 10^{-4} \text{ (M)}$$

$$\text{Pb}(\text{IO}_3)_2 : C_{\text{Pb}^{2+}(4)} \geq \frac{10^{-12.61}}{(0.001)^2} = 2.45 \times 10^{-7} \text{ (M)}$$

$$\text{PbCl}_2 : C_{\text{Pb}^{2+}(5)} \geq \frac{10^{-4.8}}{(0.05)^2} = 6.34 \times 10^{-3} \text{ (M)}$$

$C_{\text{Pb}^{2+}(2)} < C_{\text{Pb}^{2+}(4)} < C_{\text{Pb}^{2+}(1)} < C_{\text{Pb}^{2+}(3)} < C_{\text{Pb}^{2+}(5)} \rightarrow$ The order of precipitation:
 PbC_2O_4 , $\text{Pb}(\text{IO}_3)_2$, PbSO_4 , PbI_2 and PbCl_2 .



3.2 When PbI_2 begins to precipitate (assume I^- has not reacted)

$$[\text{SO}_4^{2-}] = \frac{K_s(\text{PbSO}_4)}{C_{\text{Pb}^{2+}(3)}} = \frac{10^{-7.66}}{1.47 \times 10^{-4}} = 1.49 \times 10^{-4} \text{ (M)}$$

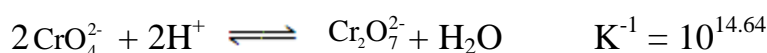
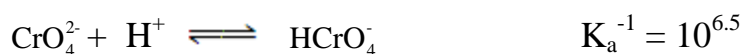
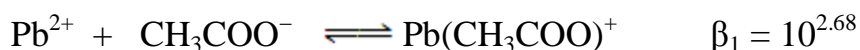
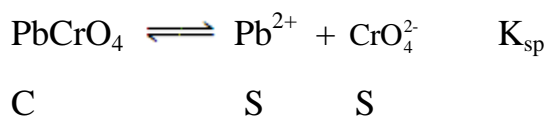
$$= \sqrt{K_s(\text{PbSO}_4)} = 1.48 \times 10^{-4} \text{ (M)} = S_{\text{PbSO}_4}$$

(S is the solubility of PbSO_4 in saturated solution). Hence PbC_2O_4 , $\text{Pb}(\text{IO}_3)_2$ and PbSO_4 have precipitated completely.

$$\begin{aligned} \rightarrow 21.60 \times C_{\text{Pb}(\text{NO}_3)_2} &= 20.00 \times (C_{\text{C}_2\text{O}_4^{2-}} + 2 \times C_{\text{IO}_3^-} + C_{\text{SO}_4^{2-}}) \\ &= 20.00(5.0 \times 10^{-3} + 2 \times 0.0010 + 0.020) \end{aligned}$$

$$\rightarrow C_{\text{Pb}(\text{NO}_3)_2} = 0.025 \text{ (M)}$$

4.



Let h be $[\text{H}^+]$, a conservation of mass requires that:

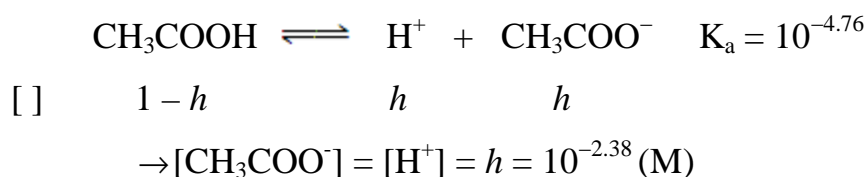
$$S = C_{\text{CrO}_4^{2-}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2 \cdot [\text{Cr}_2\text{O}_7^{2-}] = [\text{CrO}_4^{2-}](1 + K_a^{-1} \cdot h) + 2 \cdot K^{-1} \cdot h^2 \cdot [\text{CrO}_4^{2-}]^2 \quad (1)$$

$$\begin{aligned} S = C_{\text{Pb}^{2+}} &= [\text{Pb}^{2+}] + [\text{PbOH}^+] + [\text{Pb}(\text{CH}_3\text{COO})^+] + [\text{Pb}(\text{CH}_3\text{COO})_2] \\ &= [\text{Pb}^{2+}](1 + {}^*\beta h^{-1} + \beta_1[\text{CH}_3\text{COO}^-] + \beta_2[\text{CH}_3\text{COO}^-]^2) \end{aligned}$$



$$\rightarrow [\text{Pb}^{2+}] = \frac{S}{1 + \beta_1 h^{-1} + \beta_1 [\text{CH}_3\text{COO}^-] + \beta_2 [\text{CH}_3\text{COO}^-]^2} \quad (2)$$

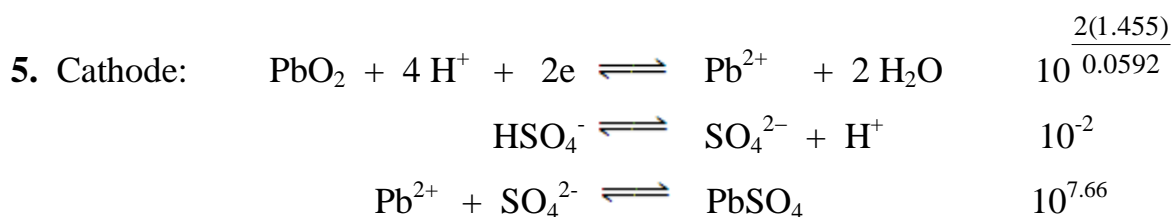
Because $S = 2.9 \times 10^{-5} \text{ M} \ll C_{\text{CH}_3\text{COOH}} = 1 \text{ M} \rightarrow \text{pH}$ of the solution is largely dependent on the dissociation of CH_3COOH :



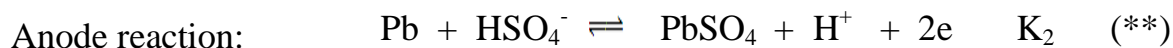
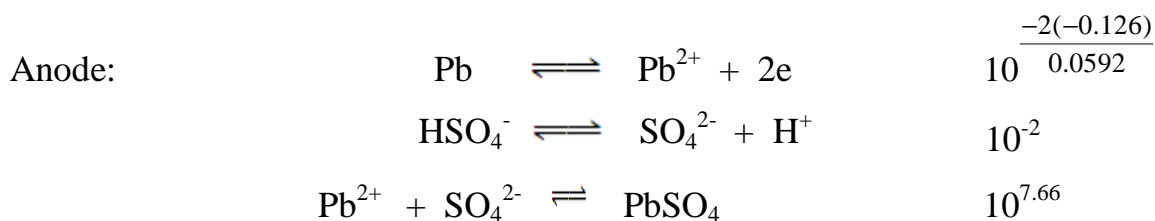
Substitute $[\text{CH}_3\text{COO}^-] = [\text{H}^+] = h = 10^{-2.38} (\text{M})$ and $S = 2.9 \times 10^{-5}$ into (1) and (2), we have:

$$[\text{CrO}_4^{2-}] = 2.194 \times 10^{-9} (\text{M}) \text{ and } [\text{Pb}^{2+}] = 9.051 \times 10^{-6} (\text{M})$$

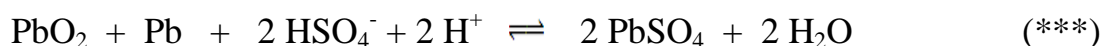
$$\rightarrow K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 1.99 \times 10^{-14}.$$



Cathode reaction:



Overall reaction as the battery discharges:





6.

$$\underline{6.1} \text{ According to (*): } 10^{\frac{2E_{\text{PbO}_2/\text{PbSO}_4}^0}{0.0592}} = K_1 = 10^{\frac{2(1.455)}{0.0592}} 10^{-2} 10^{7.66}$$

$$\rightarrow E_{\text{PbO}_2/\text{PbSO}_4}^0 = 1.62 \text{ (V)}$$

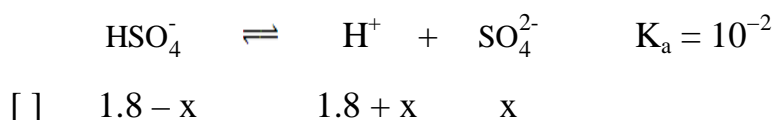
According to (**):

$$10^{\frac{-2E_{\text{PbSO}_4/\text{Pb}}^0}{0.0592}} = K_2 = 10^{\frac{-2(-0.126)}{0.0592}} 10^{-2} 10^{7.66} \rightarrow E_{\text{PbSO}_4/\text{Pb}}^0 = -0.29 \text{ (V)}$$

6.2 According to (***):

$$V = E_{(c)} - E_{(a)} = E_{\text{PbO}_2/\text{PbSO}_4}^0 - E_{\text{PbSO}_4/\text{Pb}}^0 + \frac{0.0592}{2} \log [\text{HSO}_4^-]^2 [\text{H}^+]^2$$

In which $[\text{HSO}_4^-]$, $[\text{H}^+]$ are calculated as follows:



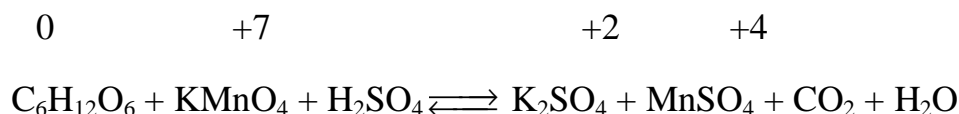
$$[\text{SO}_4^{2-}] = x = 9.89 \times 10^{-3} \text{ (M)} \rightarrow [\text{H}^+] = 1.81 \text{ (M)}; [\text{HSO}_4^-] = 1.79 \text{ (M)}$$

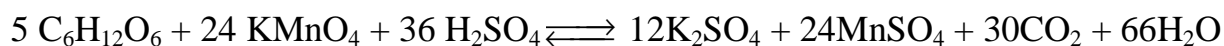
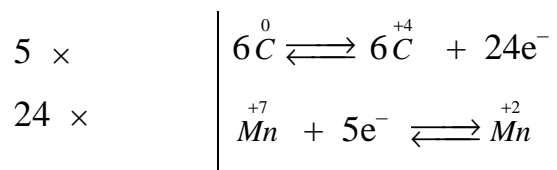
$$V = 1.62 + 0.29 + \frac{0.0592}{2} \log (1.79)^2 (1.81)^2 = 1.94 \text{ (V)}$$

Problem 10. Applied Electrochemistry

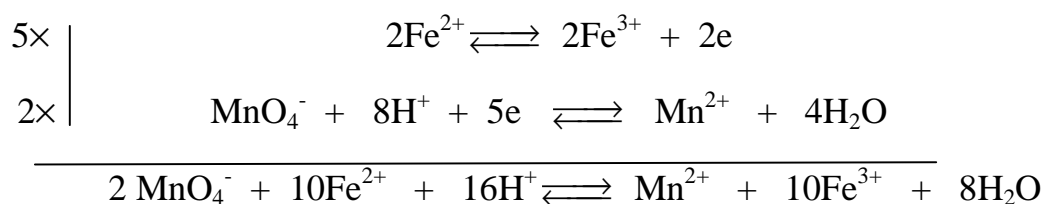
1.

1.1

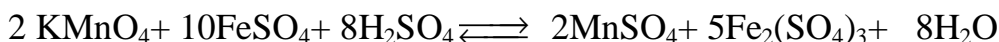




1.2



Overall reaction:



1.3

- At anode: $2 Fe^{2+} \rightleftharpoons 2 Fe^{3+} + 2e^-$

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

The cell diagram:



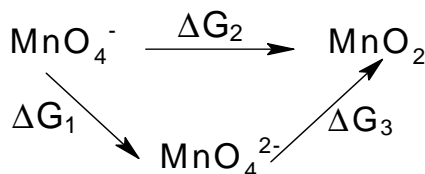
1.4 Electromotive force E of the cell can be calculated as follows:

$$E = E^0 - \frac{0.059}{5} \log \frac{[Mn^{2+}][Fe^{3+}]^5 [H_2O]^4}{[MnO_4^-][Fe^{2+}]^5 [H^+]^8}$$

2.

2.1 In order to determine the reduction potential of the pair MnO_4^{2-}/MnO_2 we need

to use the below diagram:



According to Hess' Law:



$$\Delta G_2^0 = \Delta G_1^0 + \Delta G_3^0$$

$$\Delta G_3^0 = \Delta G_2^0 - \Delta G_1^0$$

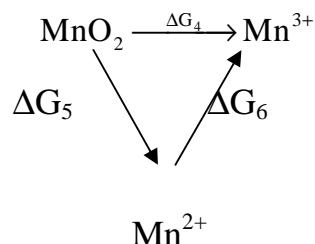
We have $\Delta G_3^0 = -nFE^0 \rightarrow E_3^0 = 2.27 \text{ V} = E_{\text{MnO}_4^{2-}/\text{MnO}_2}^0$

2.2 Similarly, we have:

$$\Delta G_4^0 = \Delta G_5^0 + \Delta G_6^0$$

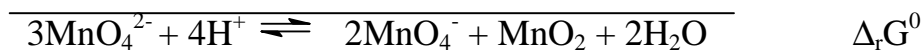
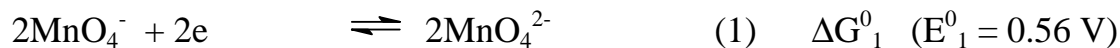
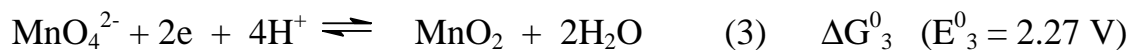
We have $\Delta G^0 = -nFE^0$.

$$\Delta E_{\text{MnO}_2/\text{Mn}^{3+}} = 0.95 \text{ V} = E_4^0$$



3.

3.1 According to the standard reduction potential diagram, we have:



3.2 In order to know if the reaction is spontaneous, ΔG must be considered.

The reaction that is considered can be obtained by subtracting (1) from (3):

$\Delta_r G^0 = \Delta G_3^0 - \Delta G_1^0$. We have $\Delta G^0 = -nFE^0$ where $\Delta E_{\text{reaction}}^0 = 1.71 \text{ V}$, or $\Delta G_3 < 0$ and the reaction is spontaneous.

3.3 The equilibrium constant can also be calculated:

$$\log K_3 = \frac{n\Delta E^0}{0.059} \rightarrow \log K_3 = \frac{2 \times 1.71}{0.059} \rightarrow K_3 = 9.25 \times 10^{57}$$

The large value of K confirms the reaction to be spontaneous.



Problem 11. Phosphoric acid

1. H^+ is used instead of H_3O^+ for clarity. The activities of the ions are ignored. $[H^+]$ is abbreviated as h in all calculations and acid constants for H_3PO_4 are written as K_1 , K_2 and K_3 .

As $K_1 \gg K_2 \gg K_3$, only first dissociation step is considered.



As

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{h^2}{C_o - h} = 10^{-2.14} = \frac{(10^{-1.14})^2}{C_o - 10^{-1.46}}$$

Solving for C_o gives $C_o = 0.200$ M

The concentrations of the forms:

$$\begin{aligned} [H_3PO_4] &= \frac{h^3 C_o}{h^3 + h^2 K_1 + h K_1 K_2 + K_1 K_2 K_3} \quad (h K_1 K_2 + K_1 K_2 K_3 \text{ is ignored}) \\ &= \frac{h^3 C_o}{h^3 + h^2 K_1} = \frac{h C_o}{h + K_1} = \frac{10^{-1.46} \times 0.2}{10^{-1.46} + 10^{-2.14}} = 0.1653 \text{ M} \end{aligned}$$

Similarly, we have:

$$[H_2PO_4^-] = \frac{h^2 K_1 C_o}{h^3 + h^2 K_1} = \frac{K_1 C_o}{h + K_1} = \frac{10^{-2.14} \times 0.2}{10^{-1.46} + 10^{-2.14}} = 0.0346 \text{ M}$$

$$[HPO_4^{2-}] = \frac{h K_1 K_2 C_o}{h^3 + h^2 K_1} = \frac{K_1 K_2 C_o}{h^2 + h K_1} = \frac{10^{-2.14} \times 10^{-7.20} \times 0.2}{(10^{-1.46})^2 + 10^{-1.46} \times 10^{-2.14}} = 6.29 \times 10^{-8} \text{ M}$$

$$[PO_4^{3-}] = \frac{K_1 K_2 K_3 C_o}{h^3 + h^2 K_1} = \frac{10^{-2.14} \times 10^{-7.20} \times 10^{-12.38} \times 0.2}{(10^{-1.46})^3 + (10^{-1.46})^2 \times 10^{-2.14}} = 7.56 \times 10^{-19} \text{ M}$$

2. We have:

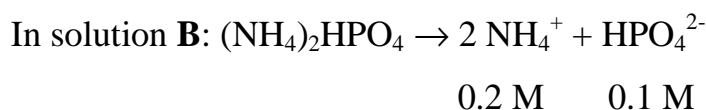


$$n_{\text{H}_3\text{PO}_4} = 0.2 \times 0.050 = 0.010 \text{ mol}$$

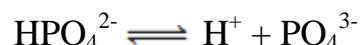
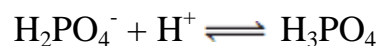
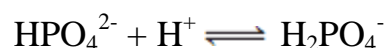
$$n_{\text{NH}_3} = 0.4 \times 0.050 = 0.020 \text{ mol}$$

Hence the following reaction occurs: $\text{H}_3\text{PO}_4 + 2 \text{NH}_3 \rightarrow (\text{NH}_4)_2\text{HPO}_4$

$$\text{And } [(\text{NH}_4)_2\text{HPO}_4] = \frac{0.010}{0.100} = 0.1 \text{ M}$$



We have the following equilibria:



A conservation of protons requires:

$$[\text{H}^+] + 2[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] = [\text{OH}^-] + [\text{PO}_4^{3-}] + [\text{NH}_3] \quad (1)$$

In which $[\text{NH}_3] + [\text{NH}_4^+] = 0.2 \text{ M}$

$$[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 0.1 \text{ M}$$

We also have:

$$[\text{NH}_3] = \frac{K_{\text{NH}_4^+} \times 0.2}{h + K_{\text{NH}_4^+}}$$

$$[\text{H}_3\text{PO}_4] = \frac{h^3 \times 0.1}{h^3 + h^2 K_1 + h K_1 K_2 + K_1 K_2 K_3}$$

$$[\text{H}_2\text{PO}_4^-] = \frac{h^2 K_1 \times 0.1}{h^3 + h^2 K_1 + h K_1 K_2 + K_1 K_2 K_3}$$



$$[\text{HPO}_4^{2-}] = \frac{hK_1K_2 \times 0.1}{h^3 + h^2K_1 + hK_1K_2 + K_1K_2K_3}$$

$$[\text{PO}_4^{3-}] = \frac{K_1K_2K_3 \times 0.1}{h^3 + h^2K_1 + hK_1K_2 + K_1K_2K_3}$$

As pH of the solution is of about 7 – 9 so we can ignore the $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{H}_3\text{PO}_4]$ and $[\text{PO}_4^{3-}]$ in the equation (1):

$$[\text{H}_2\text{PO}_4^-] = [\text{NH}_3]$$

$$\frac{h^2K_1 \times 0.1}{h^3 + h^2K_1 + hK_1K_2 + K_1K_2K_3} = \frac{K_{\text{NH}_4^+} \times 0.2}{h + K_{\text{NH}_4^+}}$$

$$\frac{h \times 0.1}{h + K_2} = \frac{h \times 0.1}{h + 10^{-7.20}} = \frac{10^{-9.24} \times 0.2}{h + 10^{-9.24}} \quad (h^3 + K_1K_2K_3 \text{ is ignored})$$

Solving for h gives $h = 8.81 \times 10^{-9}$ M and pH = 8.06.

3. Mixing of **B** and $\text{Mg}(\text{NO}_3)_2$ solution leads to precipitation reaction:



$$[\text{Mg}^{2+}] = 0.2/2 = 0.1 \text{ M}$$

As **B** is a buffer solution when it is diluted to twice the original volume, pH is virtually unchanged and is 8.06.

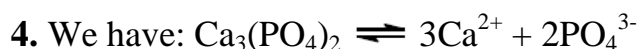
$$[\text{NH}_4^+] = \frac{hC}{h + K_{\text{NH}_4^+}} = \frac{10^{-8.06} \times 0.1}{10^{-8.06} + 10^{-9.24}} = 0.094 \text{ M}$$

$$[\text{PO}_4^{3-}] = \frac{K_1K_2K_3 \times C_o}{h^2K_1 + hK_1K_2} = \frac{K_2K_3C_o}{h^2 + hK_2} = \frac{10^{-7.20} \times 10^{-12.38} \times 0.05}{(10^{-8.06})^2 + 10^{-8.06} \times 10^{-7.20}} = 2.06 \times 10^{-8} \text{ M}$$

The ionic product:

$$[\text{NH}_4^+][\text{Mg}^{2+}][\text{PO}_4^{3-}] = 0.1 \times 0.094 \times 2.06 \times 10^{-6} = 1.93 \times 10^{-8} > 2.5 \times 10^{-13}$$

Therefore, the precipitation occurs.



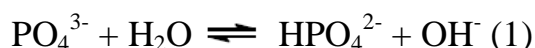


Assume that the hydrolysis of PO_4^{3-} can be ignored, the solubility S_0 of $\text{Ca}_3(\text{PO}_4)_2$ can be calculated as follows:

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3S_0)^3(2S_0)^2 = 108S_0^5 = 2.22 \times 10^{-25}$$

Solving for S_0 to gives $S_0 = 4.6 \times 10^{-6} \text{ M}$

However, the hydrolysis of PO_4^{3-} cannot be ignored due to its rather strong basicity ($\text{p}K_{\text{b}} = 14 - \text{p}K_{\text{a}} = 14 - 12.38 = 1.62$)



We can ignore the hydrolysis of HPO_4^{2-} ($\text{p}K_{\text{b}} = 14 - 7.20 = 6.80$) and H_2PO_4^- ($\text{p}K_{\text{b}} = 14 - 2.14 = 11.86$).

According to (1): $[\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 2S$ (2)

As $[\text{PO}_4^{3-}]$ is very small (the calculation above), it can be ignored in (2). It can alternatively be calculated as follows:

Let x be the concentrations of HPO_4^{2-} and OH^- , $[\text{HPO}_4^{2-}] = [\text{OH}^-] = x$

$$\text{We have: } \frac{x^2}{2 \times 4.6 \times 10^{-6} - x} = 10^{-1.62} = 0.024$$

Solving for x gives $x = 9.19 \times 10^{-6} \rightarrow [\text{PO}_4^{3-}] = 0.01 \times 10^{-6} \text{ M}$

Therefore we can assume that $[\text{HPO}_4^{2-}] = [\text{OH}^-] = 2S$ and $[\text{PO}_4^{3-}]$ is determined based on K_3 :

$$K_3 = 10^{-12.38} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = \frac{10^{-14}}{[\text{OH}^-]} \times \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$\Rightarrow [\text{PO}_4^{3-}] = \frac{10^{-12.38} \times 2S}{10^{-14}} = 167S^2$$

The solubility S of $\text{Ca}_3(\text{PO}_4)_2$: $K_{\text{sp}} = 2.25 \times 10^{-25} = (3S)^3(2 \times 167S^2)^2 = 3012012S^7$

$$\Rightarrow S = 3.6 \times 10^{-5} \text{ M.}$$

We can see that solubility of $\text{Ca}_3(\text{PO}_4)_2$ increases about 10 times due to the hydrolysis of PO_4^{3-} .

Note: Students may use logarithmic concentration diagram to get the relationship $[\text{HPO}_4^{2-}] = [\text{OH}^-] = 2S$.

Problem 12. Kinetic Chemistry

1. To determine $t_{1/2}$, the time taken from the initial concentration of N_2O_5 ($3.80 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) to fall to one-half of its value:

$t_{1/2} \approx 180 \text{ s}$ corresponding to $[\text{N}_2\text{O}_5]_{t_{1/2}} = 1.90 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

2.

2.1

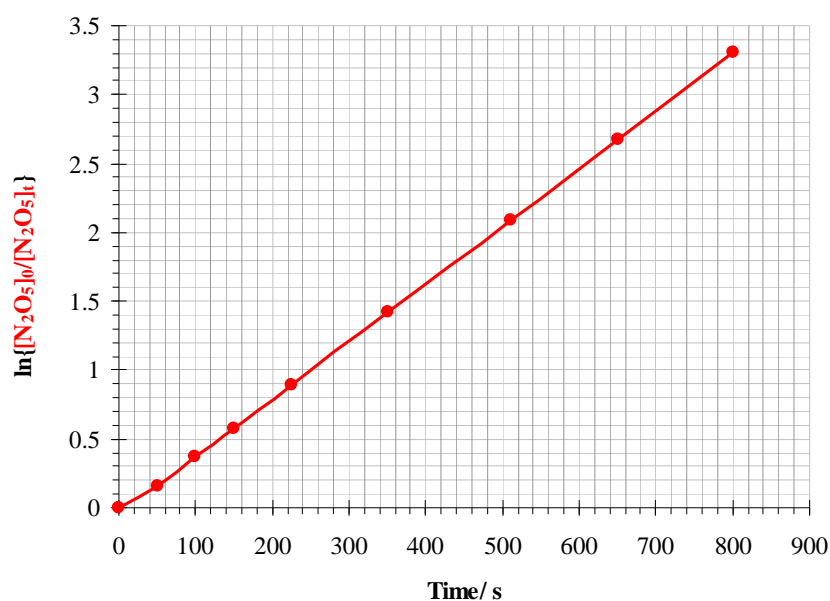


Figure 2. A re-plot of the data in Figure 1 as function of $\ln \{[\text{N}_2\text{O}_5]_0/[\text{N}_2\text{O}_5]_t\}$ versus time

The plot of $\ln \{[\text{N}_2\text{O}_5]_0/[\text{N}_2\text{O}_5]_t\}$ versus time is linear for a first order reaction.

2.2 $r = k [\text{N}_2\text{O}_5]$

The form of integrated rate equation:

$$\ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = kt \quad \text{or} \quad [\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 e^{-kt}$$

3. The 1st order reaction:

$$k = \ln 2 / t_{1/2} = \ln 2 / 180 \text{ s} = 3.85 \times 10^{-3} \text{ s}^{-1}$$



4.

E_a is independent of temperature:

$$\ln \frac{k_{336.6K}}{k_{318K}} = \frac{E_a}{R} \left[\frac{1}{318} - \frac{1}{336.6} \right] \Rightarrow \ln \frac{3.85 \times 10^{-3}}{5.02 \times 10^{-4}} = \frac{E_a}{8.314 J / mol.K} [3.145 \times 10^{-3} - 2.97 \times 10^{-3}]$$

$$E_a = \mathbf{97.46 \text{ kJ}}$$

Pre-exponential factor (A):

$$k = A \cdot e^{-E_a/RT} \text{ at } 336.3 \text{ K, } A = k \cdot e^{E_a/RT} = 3.85 \times 10^{-3} e^{97460/8.3145 \times 336.3} = \mathbf{5.28 \times 10^{12} \text{ s}^{-1}}.$$

5. The intermediate concentrations can be treated by the steady-state approximation:

$$r_{NO} = \frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \rightarrow [NO] = \frac{k_2[NO_2]}{k_3} \quad (\text{Eq.1})$$

Substituting this equation into the below equation:

$$r_{NO_3} = \frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \quad (\text{Eq. 2})$$

$$\rightarrow k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3 \frac{k_2[NO_2]}{k_3} [NO_3] = 0$$

$$\rightarrow k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - 2k_2[NO_2][NO_3] = 0$$

$$\rightarrow \frac{k_1[N_2O_5]}{k_{-1} + 2k_2} = [NO_2][NO_3] \quad (\text{Eq.3})$$

The reaction rate:

$$\begin{aligned} r_2 = r_{N_2O_5} &= -\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] \\ &= k_1[N_2O_5] - k_{-1} \frac{k_1[N_2O_5]}{k_{-1} + 2k_2} \\ &= \frac{2k_1k_2}{k_{-1} + 2k_2} [N_2O_5] \\ &= k[N_2O_5] \end{aligned}$$



Problem 13. Kinetics of the decomposition of hydrogen peroxide

1. Chemical reaction: $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$

The reaction rate is proportional to the volume of oxygen gas released in a unit of time.

In experiments #1, #2, and #3 when the volume of H_2O_2 solution doubles while keeping the same volume of KI solution, the reaction rate also doubles. Therefore, the rate is directly proportional to the concentration of H_2O_2 . Hence, the reaction is the first-order with the respect to H_2O_2 .

Similarly, from experiments #2, #4, and #5 the rate is directly proportional to the concentration of I^- . Hence, the reaction is the first-order with the respect to I^- .

2. Chemical reaction: $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$

The rate law: $v = kC_{\text{H}_2\text{O}_2}C_{\text{I}^-}$

3. In the experiment #4, the solution of H_2O_2 is diluted three times; therefore, the concentration of H_2O_2 was reduced three times.

$$C_0 = 10 \text{ g H}_2\text{O}_2 / 1 \text{ L} = 10/34 = 0.294 \text{ M.}$$

Because the reaction proceeds slowly, the reaction rate (or the rate of releasing oxygen gas) is considered to be unchanged after of short period of time (4 min).

The volume of oxygen released after 4 min is equal to $4.25 \times 4 = 17 \text{ (mL O}_2\text{)}$.

$$\text{Hence, } n_{\text{O}_2} = \frac{PV}{RT} = \frac{(1)(17 \times 10^{-3})}{(0.082)(298)} = 0.695 \times 10^{-3} \text{ (mol)}$$

$$\text{At the beginning, } n_{\text{H}_2\text{O}_2} = (0.294)(0.15) = 44.1 \times 10^{-3} \text{ (mol)}$$

$$\text{After 4 min, } n_{\text{H}_2\text{O}_2} = 44.1 \times 10^{-3} - 2(0.695 \times 10^{-3}) = 42.71 \times 10^{-3} \text{ (mol)}$$

$$\text{Therefore, after 4 min } C_{\text{H}_2\text{O}_2} = \frac{0.04271}{0.15} = 0.285 \text{ M.}$$

4. The overall reaction: $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$ (*)



$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt}$$

Consider three different cases:

a) If step (1) is slow and determines the overall rate, the rate of the overall reaction (*) will be the same as the rate of step (1):

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = k_1[H_2O_2][I^-]$$

which corresponds to the overall rate law as determined in section 2.

b) If step (2) is slow, hence

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = k_2[H_2O_2][IO^-] \quad (a)$$

Assume that the steady-state approximation is applied for IO^- , we have

$$\frac{d[IO^-]}{dt} = k_1[H_2O_2][I^-] - k_2[IO^-][H_2O_2] = 0 \rightarrow [IO^-] = \frac{k_1}{k_2}[I^-] \quad (b)$$

Replace $[IO^-]$ from (b) in (a), we have:

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = k_1[H_2O_2][I^-]$$

which is also appropriate to the overall rate law.

c) If the two steps have similar rates:

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = \frac{1}{2} (k_1[H_2O_2][I^-] + k_2[H_2O_2][IO^-])$$

Let us assume that the concentration of IO^- is in steady-state condition. Similar to the case b), we have:

$$v = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = k_1[H_2O_2][I^-]$$

which corresponds to the overall rate law.

Among the three cases, case a) is the most appropriate to the overall rate law because no assumption is made. Besides, in the case b) the assumption of the steady-state IO^- is not valid since the step (2) is considered slow.



Problem 14. Magnetism of transition metal complexes

1. Two compounds are octahedral complexes of Mn^{2+} (d^5).

1.1 $\text{K}_4[\text{Mn}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ is low spin, 1 unpaired electron.

$\text{K}_4[\text{Mn}(\text{SCN})_6]$ is high spin, 5 unpaired electrons.

1.2 CN^- is strong field ligand, electronic configuration is $(t_{2g})^5(e_g)^0$

SCN^- is weak field ligand, electronic configuration is $(t_{2g})^3(e_g)^2$

2. Ni^{2+} (d^8) in octahedral field has electronic configuration of $(t_{2g})^6(e_g)^2$ with two unpaired electrons. The spin only χ_{eff} is 2.83 MB.

3.
$$\mu_{\text{eff}} = 2.83 \times \left(1 - \frac{4(-315)}{8500} \right) \text{ (BM)}$$

Thus, μ_{eff} is 3.25 MB

4.

4.1 d^8 in square planar field is diamagnetic.

4.2 **C** is neutral, DBM is monoanionic form. $M_c = 504$ (g/mol). **A** should be hydrate form of **C**, $M_A = M_B / 0.932 = 540.8$ (g/mol), corresponding to two molecules of H_2O per $[\text{Ni}(\text{DBM})_2]$. Thus, the formula is $[\text{Ni}(\text{DBM})_2] \cdot 2\text{H}_2\text{O}$

4.3 Water should coordinate to Ni center due to the change of color and magnetic property. μ_{eff} value of **A** is close to that of $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$. So, an octahedral complex is expected for **A**.

4.4 There are three isomers, the *trans* isomer and two optical *cis* isomers.

4.5 **B** should be an octahedral complex, due to the color and magnetic moment are similar to those of **A**. Octahedral geometry can be formed by oligomerization / polymerization of **B** on heating, the DBM may play as bridging ligand.



Problem 15. Structure and synthesis of Al-Keggin ion

1.

1.1 Al_2Cl_6 has sp^3 hybridization

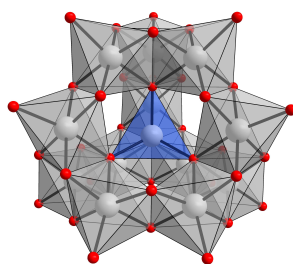
1.2 $\text{Al} - \text{Al} = \frac{2x(\text{Al} - \text{Al})}{2} = 2(\text{Al} - \text{Cl}) \cos(39.5^\circ) = 2 \times 221 \text{ pm} \times 772 = 325.63 \text{ pm}$

2.

2.1 $n = 7+$

2.2 The $\text{Al}_{\text{octahedral}}/\text{Al}_{\text{tetrahedral}}$ is estimated $\sim 12/1$. The center Al atom at number 7 is tetrahedral; the other atoms are octahedral.

2.3 and 2.4 The Al-Keggin cation structure is composed of one $\text{Al}_{\text{tetrahedral}}$ cation surrounded by four oxygens. This Al atom is located centrally and caged by 12 octahedral AlO_6 -units linked to one another by the neighboring oxygen atoms. There are a total of 24 bridging oxygen atoms that link the 12 adjacent atoms. The cations centered in the 12 octahedra are arranged on a sphere almost equidistant from each other. The formula can be expressed as $(\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12})^{7+}$.



(with the permission of Aleksandar Kondinski, Jacobs University)

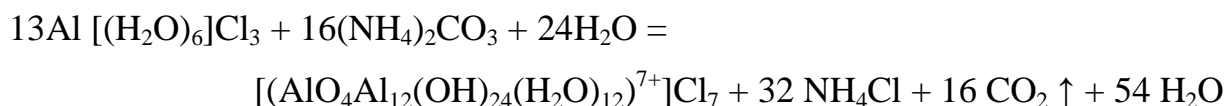
2.5



3.



3.1



3.2 Volume of a ball = $(4/3) \pi r^3 = (4/3) \times 3.14 \times (0.542)^3 = 0.667 \text{ cm}^3$.

Volume of 3 balls = $3 \times 0.667 = 2.00 \text{ cm}^3$.

Inner volume of crucible = 15 cm^3

Volume of gas = $15 - 2 = 13 \text{ cm}^3$.

$PV = nRT \rightarrow n = 1 \times 13 \times 10^{-3} / 0.082 \times 298 = 5.32 \times 10^{-4} \text{ mol}$.

After reaction:

$$\sum n_{\text{gases}} = n_{\text{before}} + n_{\text{CO}_2}$$

$PV = n_{\text{gases}}RT \rightarrow n = (2.50 \text{ atm}) \times (13.10^{-3} \text{ L}) / (0.082 \text{ L.atm.mol}^{-1}.\text{K}^{-1}) \times (298 \text{ K}) =$
 $1.33 \times 10^{-3} \text{ mol}$

$$n_{\text{CO}_2} = n_{\text{after}} - n_{\text{before}} = 1.33 \times 10^{-3} - 5.23 \times 10^{-4} = 8 \times 10^{-4} \text{ mol}$$

Molar number of Al_{13} -Keggin cation = $8 \times 10^{-4} / 16 = 5 \times 10^{-5} \text{ mol}$.

Number of Al_{13} -Keggin cations

$$= 5 \times 10^{-5} \text{ mol} \times 6.023 \times 10^{23} = 3 \times 10^{19} \text{ ionic molecules}$$



Problem 16. Safrole

1.

Reaction	Balanced equation
1	$\text{K}[\text{PtCl}_3\text{C}_2\text{H}_4] + \text{C}_{10}\text{H}_{10}\text{O}_2 \rightarrow \text{K}[\text{PtCl}_3(\text{C}_{10}\text{H}_{10}\text{O}_2)] + \text{C}_2\text{H}_4$
2	$2 \text{K}[\text{PtCl}_3(\text{C}_{10}\text{H}_{10}\text{O}_2)] \rightarrow [\text{Pt}_2\text{Cl}_2(\text{C}_{10}\text{H}_9\text{O}_2)_2] + 2 \text{KCl} + 2 \text{HCl}$
3	$[\text{Pt}_2\text{Cl}_2(\text{C}_{10}\text{H}_9\text{O}_2)_2] + 2 \text{C}_5\text{H}_5\text{N} \rightarrow 2 [\text{PtCl}(\text{C}_{10}\text{H}_9\text{O}_2)(\text{C}_5\text{H}_5\text{N})]$

2.

	in A	in B	in C
From the IR data	C9 and C10 bond with Pt	C9 and C10 bond with Pt	C9 and C10 bond with Pt
From the ^1H NMR data	safrole coordinated with Pt	safrole lost H5, C5 bonds with Pt	safrole lost H5, C5 bonds with Pt

3.

A	B	C

4.

Reaction	Driving force
1	$\text{K}[\text{PtCl}_3\text{C}_2\text{H}_4] + \text{C}_{10}\text{H}_{10}\text{O}_2 \rightarrow \text{K}[\text{PtCl}_3(\text{C}_{10}\text{H}_{10}\text{O}_2)] + \text{C}_2\text{H}_4 \uparrow$



	Ethylene (C ₂ H ₄ , gas) is more volatile than safrole (C ₁₀ H ₁₀ O ₂ , liquid).
2	$2 \text{K}[\text{PtCl}_3(\text{C}_{10}\text{H}_{10}\text{O}_2)] \rightarrow [\text{Pt}_2\text{Cl}_2(\text{C}_{10}\text{H}_9\text{O}_2)_2] + 2 \text{KCl} + 2 \text{HCl}$ The chelate complex $[\text{Pt}_2\text{Cl}_2(\text{C}_{10}\text{H}_9\text{O}_2)_2]$ is more stable.
3	$[\text{Pt}_2\text{Cl}_2(\text{C}_{10}\text{H}_9\text{O}_2)_2] + 2 \text{C}_5\text{H}_5\text{N} \rightarrow 2 [\text{PtCl}(\text{C}_{10}\text{H}_9\text{O}_2)(\text{C}_5\text{H}_5\text{N})]$ In the dinuclear complex $[\text{Pt}_2\text{Cl}_2(\text{C}_{10}\text{H}_9\text{O}_2)_2]$, two bridging Cl weakly bond with Pt but in $[\text{PtCl}(\text{C}_{10}\text{H}_9\text{O}_2)(\text{C}_5\text{H}_5\text{N})]$ the ligand C ₅ H ₅ N strongly bonds with Pt.

5. This reaction was controlled by steric effects rather than the *trans* effect.



Problem 17. Imidazole

1.

	Structure	aromatic or not
Imidazole ($C_3H_4N_2$)		aromatic
Imidazol-1-ide anion ($C_3H_3N_2$)		aromatic
Imidazolium cation ($C_3H_5N_2$)		aromatic
Oxazole (C_3H_3NO)		aromatic
Thiazole (C_3H_3NS)		aromatic

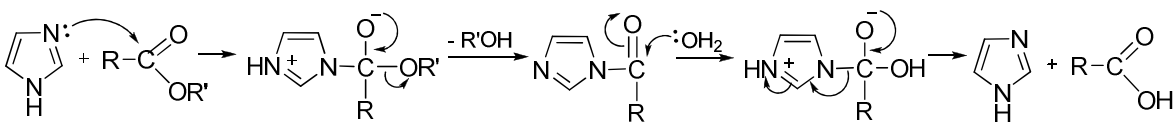
2.

Melting point	Imidazole > Thiazole > Oxazole
Justification	Imidazole is the first because of intermolecular hydrogen bonding. Thiazole is placed before oxazole because thiazole's molecular mass and polarizability are larger than those of oxazole.
Boiling point	Imidazole > Thiazole > Oxazole
Justification	Imidazole is the first because of intermolecular hydrogen bonding. Thiazole is placed before oxazole because thiazole's molecular mass and polarizability are larger than those of oxazole.

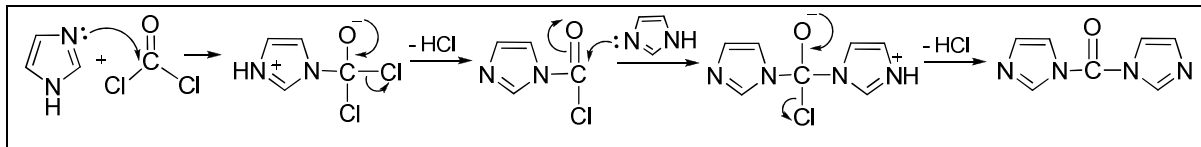
3.

Equation for the ionization	$\text{Imidazole} + \text{H-OH} \rightleftharpoons \text{Imidazolium}^+ + \text{HO}^-$ $\text{Oxazole} + \text{H-OH} \rightleftharpoons \text{Oxazolium}^+ + \text{HO}^-$ $\text{Thiazole} + \text{H-OH} \rightleftharpoons \text{Thiazolium}^+ + \text{HO}^-$
K_b	Imidazole > Thiazole > Oxazole
Justification	Conjugate acid of imidazole is symmetrical delocalized, forms stronger hydrogen bonding with water, i.e. more stable, thus imidazole more basic than oxadiazole and thiazole. Atom O is more electronegative than N and S, it decreased electron density at N of oxazole, decreased stability of oxazole's conjugate acid making oxazole less basic than thiazole.

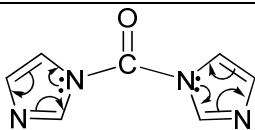
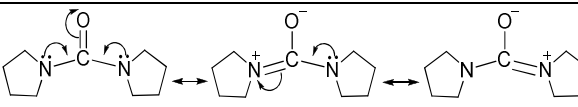
4.

Reaction mechanism:

Explanation: Atom N-3 (N at 3-position) is strong nucleophile; The positive charge is delocalized; The imidazole is good leaving group.

5.



6.

	
<p>The pair of electrons from N-1 and four electrons of the remaining four atoms form a sextet of π-electron of aromatic system. They do not conjugate with C=O, thus do not affect the bond order of C=O.</p>	<p>The pair of electrons from N-1 conjugate with C=O decreasing the bond order of C=O, hence decrease its IR stretching frequency.</p>

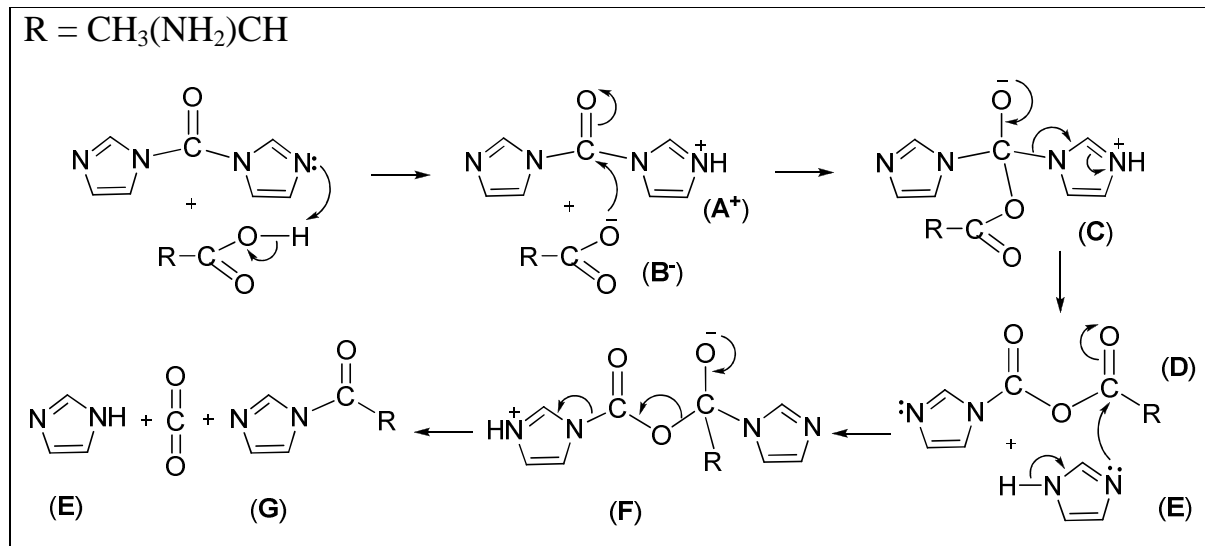
7.

$4 \text{C}_3\text{H}_4\text{N}_2 + \text{COCl}_2 \rightarrow (\text{C}_3\text{H}_3\text{N}_2)_2\text{CO} + 2 [\text{C}_3\text{H}_5\text{N}_2]\text{Cl} \quad (1)$ <p>2 mol of imidazole react with 1 mol of phosgene to form 1 mol of CDI and 2 mol of HCl; the other 2 mol of imidazole are used to react with the HCl.</p>
$2 \text{C}_3\text{H}_4\text{N}_2 + \text{COCl}_2 + 2 \text{NaOH} \rightarrow (\text{C}_3\text{H}_3\text{N}_2)_2\text{CO} + 2 \text{NaCl} + 2 \text{H}_2\text{O} \quad (2)$ <p>In imidazolyl groups of CDI the pair of electrons from N-1 and four electrons of the remaining four atoms form a sextet of π-electron of aromatic system. They do not conjugate with C=O. Two electron-withdrawing imidazolyl groups make C=O more active, the imidazole is good leaving group, hence CDI readily reacts with water from reaction (2):</p> $(\text{C}_3\text{H}_3\text{N}_2)_2\text{CO} + \text{H}_2\text{O} \rightarrow 2 \text{C}_3\text{H}_4\text{N}_2 + \text{CO}_2 \quad (3)$

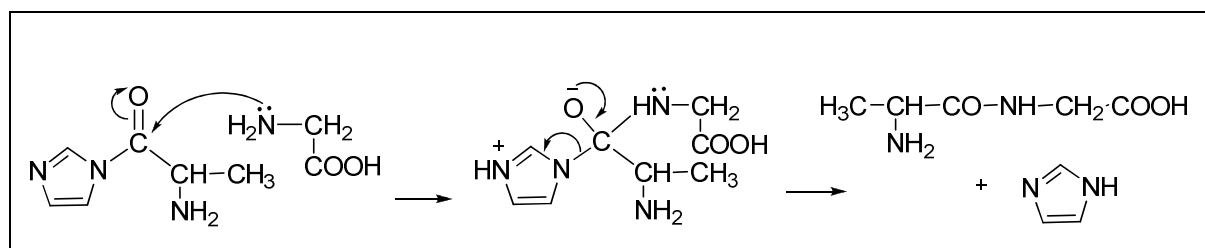
8.

8.1

$R = \text{CH}_3(\text{NH}_2)\text{CH}$



8.2

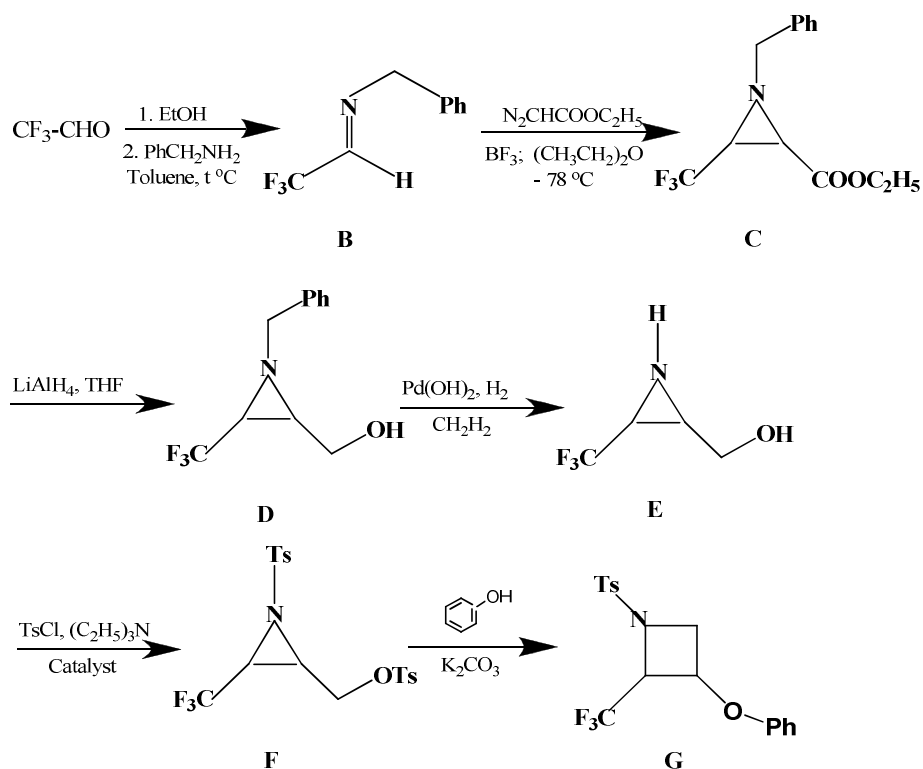




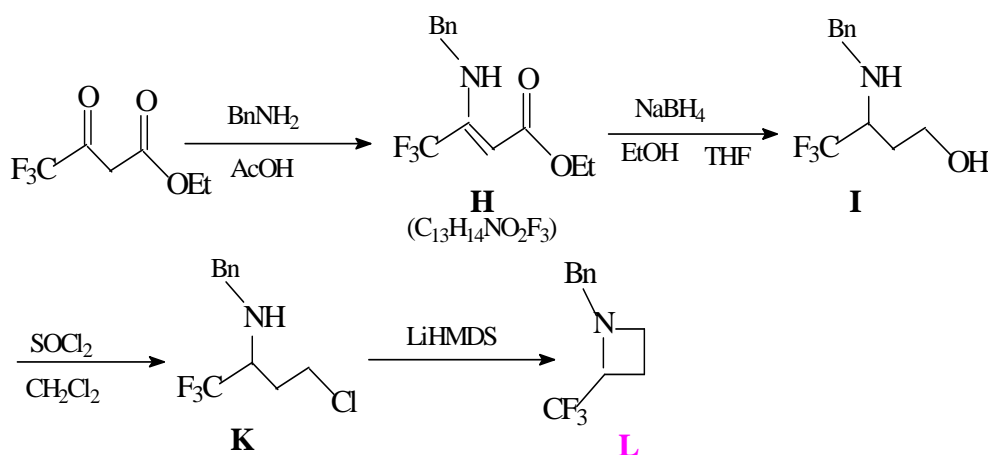
Problem 18. Small heterocycles

1.

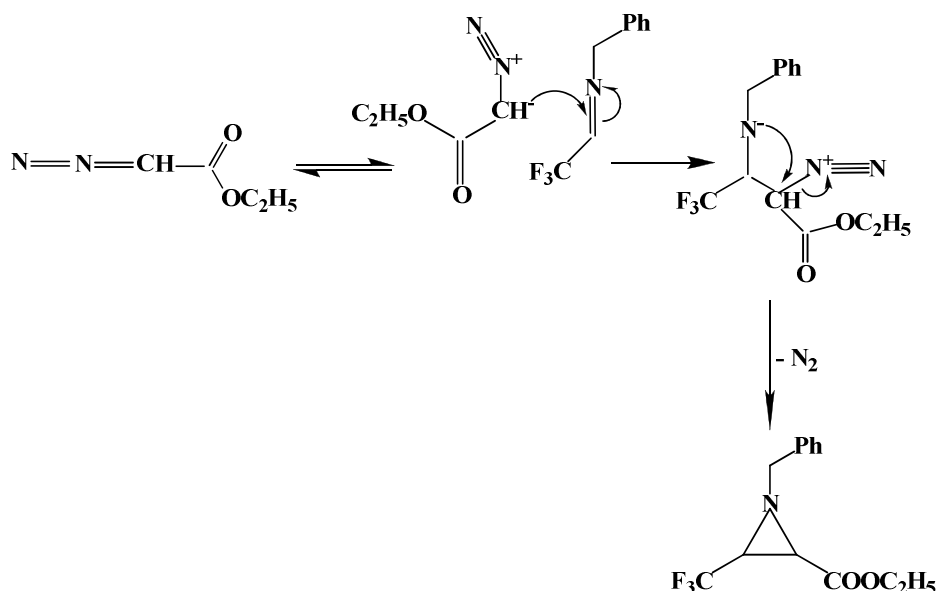
Scheme 1:



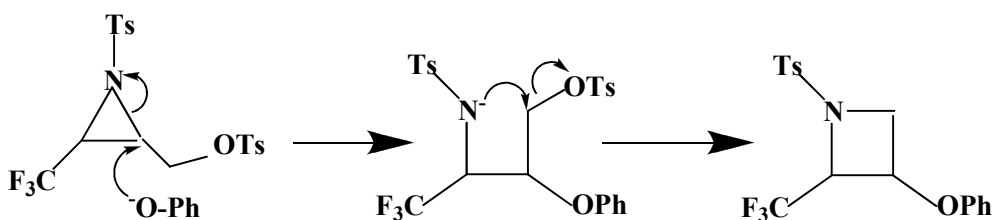
Scheme 2:



2. Reaction mechanism for the transformation from **B** to **C**:



3. Reaction mechanism for the transformation from **F** to **G**:



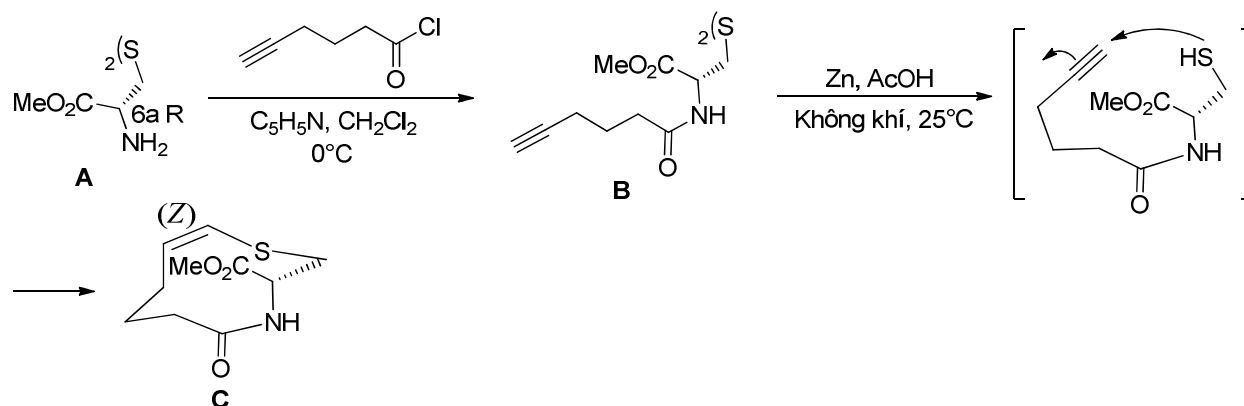
Problem 19. Vitamin H

1. The chloride acid was reacted with the amino group of the “bis(L-cystein)” (**A**) to give amide (**B**). Zn powder in acetic acid solution reduced the S-S bond of (**B**) to give an intermediate containing a thiol (-SH) group. Under normal condition, the -SH group added spontaneously to the terminal alkyne group to yield (**C**) with a ten-membered ring, of which the newly formed C=C double bonds had (Z) configuration.

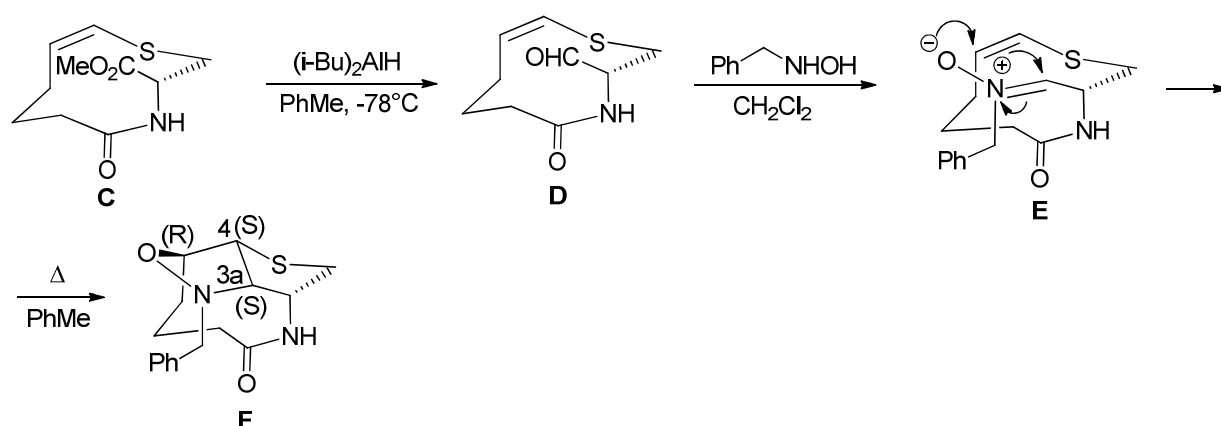


46th International Chemistry Olympiad
Hanoi, Vietnam – 2014

Preparatory Problem
Solutions

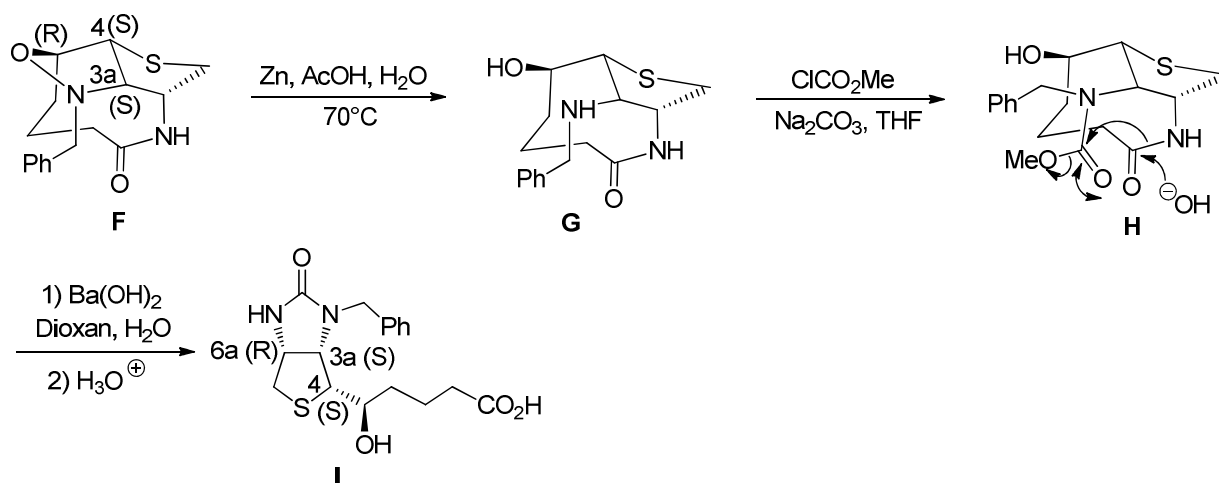


2. Diisobutyl aluminium hydride (DIBAL) partially reduced ester (C) into aldehyde (D) which was condensed with benzylhydroxylamine to give nitrone (E) with (*E*) configuration. In the intramolecular [4+2] cyclization reaction of (E) (*note that '4' and '2' are the numbers of π electron of the nitrone and the double bond involved in the cyclization, respectively*), the configuration of the double bonds C=C and C=N remained unchanged. The resulting compound (F) had three new chiral centers, two of which were (3*aS*, 4*R*). They were the configurations of the corresponding C3 and C4 in the skeleton of (*D*)-(+)-Biotin. The third chiral carbon which was attached to the oxygen atom had an (*R*) configuration.

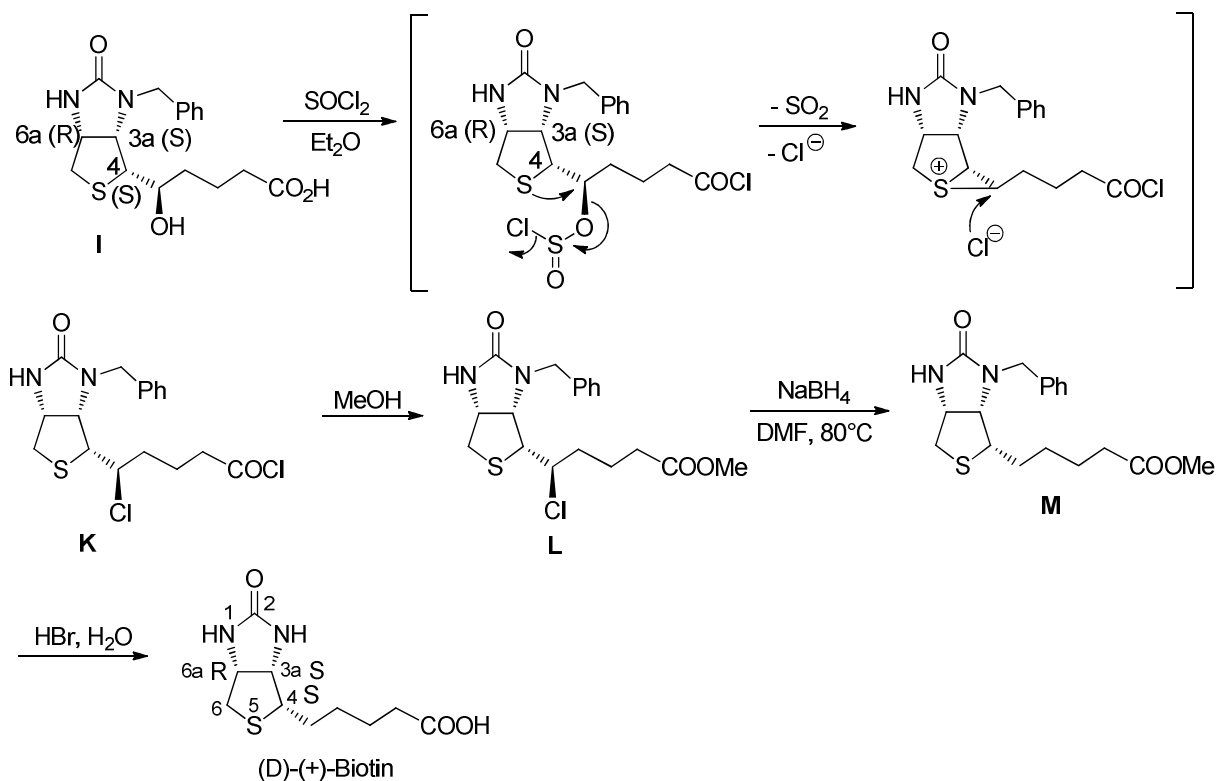


3. (F) was reduced by Zn in acetic acid to give (G) containing one –OH group and a second-order amino group. The amino group was reacted with chlorofomate in the

presence of Na_2CO_3 in THF solution produce (**H**). Under basic condition, the ten-membered ring of (**H**) was opened to give δ -hydroxy acid (**I**). The configuration ($6aR$) of (**I**) resulted from the (R) configuration of the chiral carbon in L-cysteine. Therefore, L-cystein is chosen as the starting material for the synthesis.

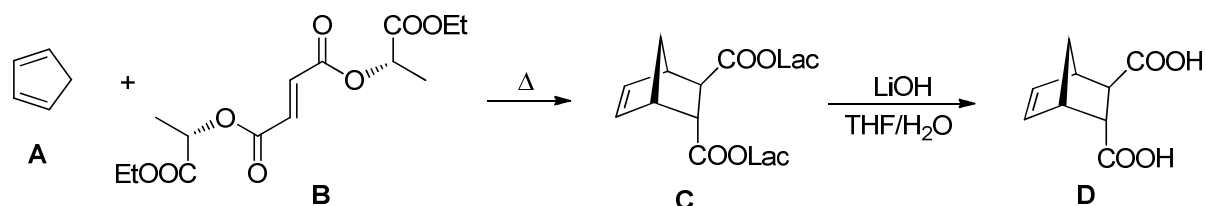


4. The sulfur atom caused an anchimeric effect by which the configuration of the carbon attached to the $-\text{OH}$ in compound (**I**) remained unchanged as this $-\text{OH}$ group was replaced by the halogen atom to yield (**K**). The halogen atom was then replaced when (**K**) was reduced with NaBH_4 in which the “pentanoic acid” branch of (*D*)-(+)-biotin was formed. The hydrolysis of ester (**M**) in the aqueous solution of HBr , followed by the removal of the benzyl group resulted in the formation of the target molecule, (*D*)-(+)-Biotin.

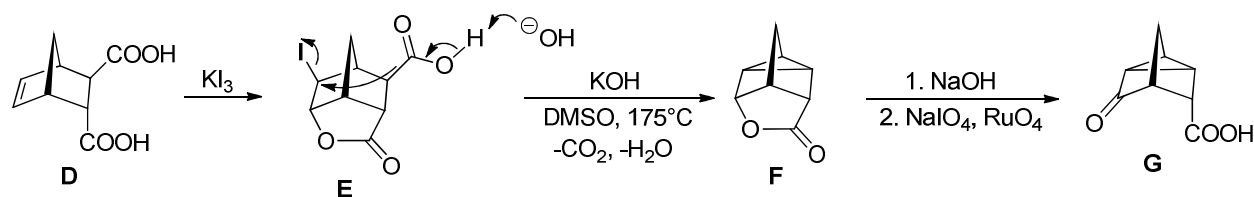


Problem 20. No perfume without jasmine

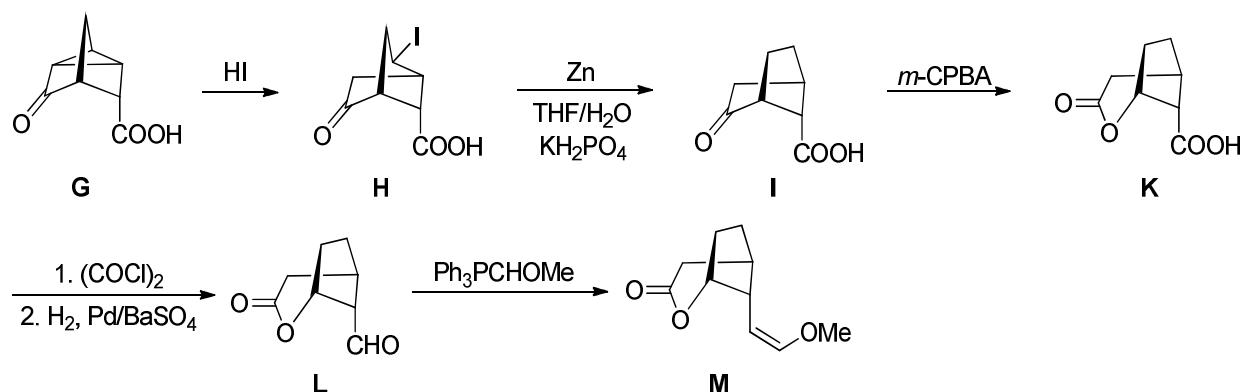
1. In a [4+2] cycloaddition reaction (Diels-Alder reaction), the configuration of the dienophile (**B**) remained unchanged: the two ester groups $-\text{COOLac}$ of compound (**C**) were placed in different sites in comparison to the six-membered ring. The hydrolysis of these two ester groups in LiOH solution gave the two corresponding *trans* carboxyl groups.



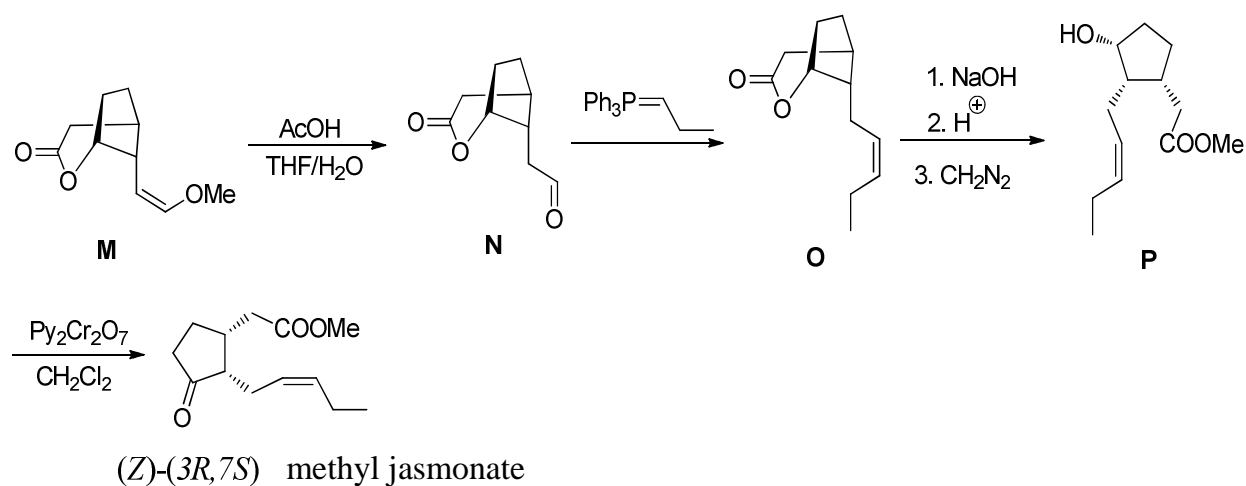
2. When dicarboxylic acid (**D**) was treated with I₂/KI, it was transformed into γ -iodolactone (**E**) of the *endo* –COOH. This lactone then underwent a decarboxylation-cyclization in basic solution step to give lactone (**F**) containing a three-membered ring. The secondary –OH group which resulted from the hydrolysis of (**F**) was oxidized by NaIO₄ to form a carbonyl group.



3. The addition-ring opening step of the cyclopropane ring with HI oriented by the (-C) conjugation effect of the carbonyl resulted in the formation of γ -iodo acid (**H**) containing only five-membered rings. The reductive elimination of the iodine atom by Zn in acetic acid produced ketoacid (**I**) which underwent a Bayer-Viiliger oxidation to yield lactone (**K**) (the main product) with one carboxyl group. The carboxyl group was treated under Rosenmund reduction condition in which lactone (**L**) with an aldehyde functional group was obtained. Vinyl ether (**M**) was separated from the Wittig reaction between the aldehyde and the ylide Ph₃P=CHOMe.



4. Methyl vinyl ether (**M**) was hydrolyzed in acidic medium to give lactone (**N**) containing an aldehyde functional group. From the Wittig reaction between (**N**) and the ylide $\text{Ph}_3\text{P}=\text{CHCH}_2\text{CH}_3$, lactone (**O**) with a *cis* carbon-carbon double bond was separated. The hydrolysis of the lactone (**O**) followed by treatment with diazomethane produced ester (**P**) which was oxidized with pyridine dichromate to give the target compound (*Z*)-(3*R*,7*S*)-methyl jasmonate.





Problem 21. Vietnamese cinnamon

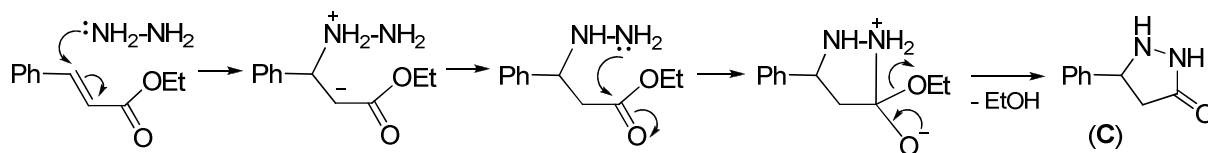
1. Give the structure for **A**, **B**, **C**.

A	B	C

2. Assign ¹H NMR signals in first spectrum to appropriate proton groups of **C**.

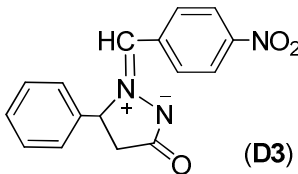
C	9.0 ppm, s	7.4-7.3 ppm, m	5.5 ppm, s	4.2 ppm, t	2.8 ppm, dd	2.6 ppm, dd
	H_e	C₆H₅	H_d	H_c	H_a	H_b

3. Propose a reaction mechanism for the formation of **C** from **B**.

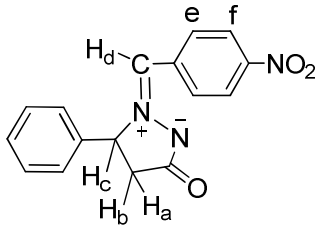




4. Among four given below structures, select one for **D** and give the reasons for your selection.

The structure for D	Reasons for your selection.
	<p>D3 derives from C and corresponds with the given ^1H NMR spectrum.</p> <p>D1 and D4 do not derive from C.</p> <p>D1 does not correspond with second ^1H NMR spectrum (For example in the spectrum there are not two ethylenic protons).</p> <p>D2 and D4 seem corresponding to the given ^1H NMR spectrum, but D2 contains three members and D4 contains four members cycles, which cannot exist after reflux for 12 h.</p>

5. Assign ^1H NMR signals in second spectrum to appropriate proton groups of **D**.

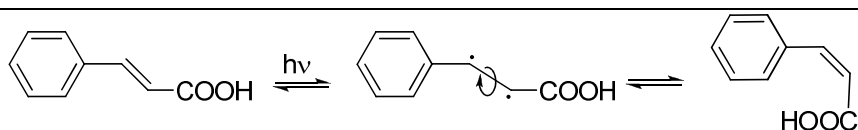
D	9.6 ppm, s	8.3 ppm, d	7.6 ppm, d	7.4- 7.3 ppm, m	3.0 ppm, t	2.9 ppm, dd	2.6 ppm, dd
	H_d	2 H_f	2 H_e	C₆H₅	H_c	H_a	H_b

Problem 22. Cinnamic acid

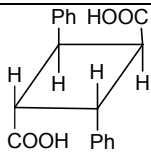
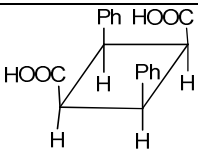
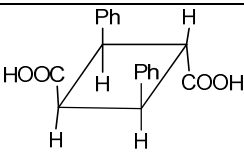
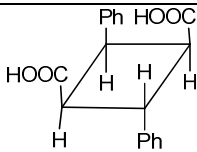
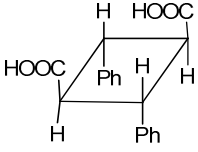
1.

1.1

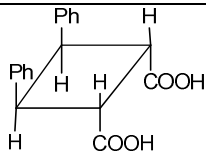
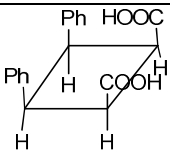
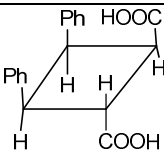
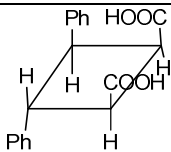
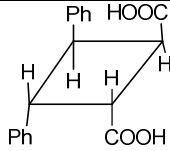
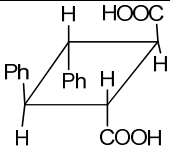
Reaction mechanism for the isomerization



1.2

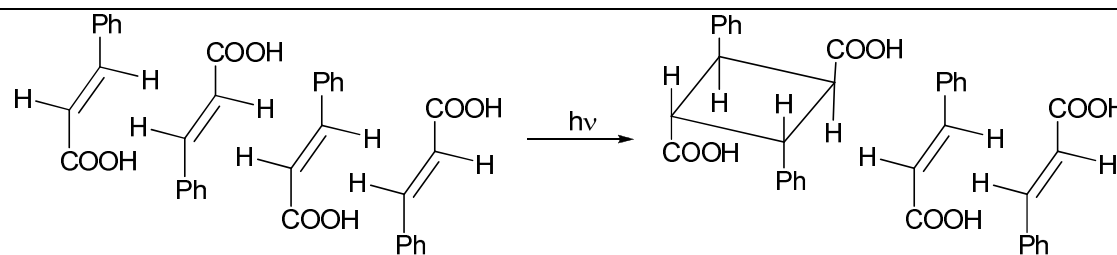
 <p>α-truxillic acid</p>			
			

1.3

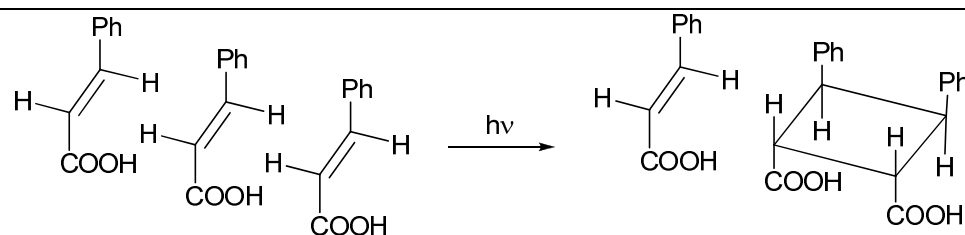
			
β -truxinic acid		Has an enantiomer	Has an enantiomer
			
Has an enantiomer	Has an enantiomer		

1.4

The packing arrangement of α -type of *trans*-cinnamic acid which led to the formation of α -truxillic acid



The packing arrangement of β -type of *trans*-cinnamic acid which led to the formation of β -truxinic acid

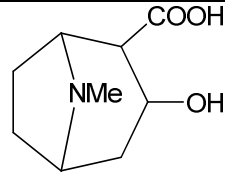
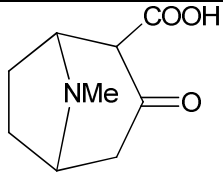
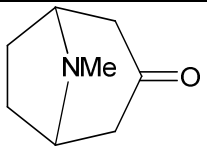


1.5

In solution all molecules of cinnamic acid were solvated and randomly arranged.

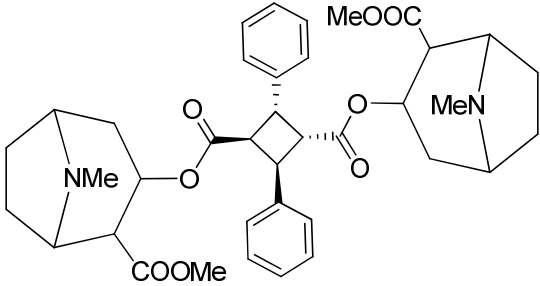
2.

2.1

A	B	C
		
Optically active since A has four asymmetric carbons and has no	Optically active since B has three asymmetric carbons and has no symmetrical	Optically inactive since C has symmetrical plane although has two

symmetrical plane and no symmetrical center.	plane and no symmetrical center.	asymmetric carbons.
--	----------------------------------	---------------------

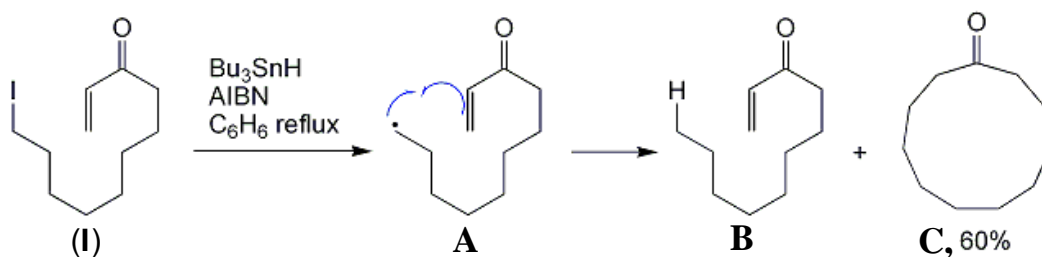
2.2

	Optical active since each bicyclooctane moiety has four asymmetric carbons and their configurations are exactly the same as in A thus α -truxilline has no symmetrical plane and no symmetrical center.
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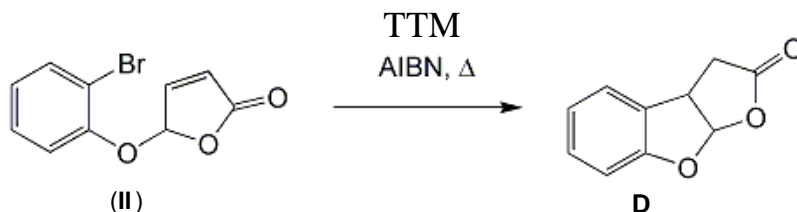
Problem 23. Tris(trimethylsilyl)silane and azobisisobutyronitrile

The products from the each reaction:

2.1 **A**, **B** and **C** from the compound (**I**):

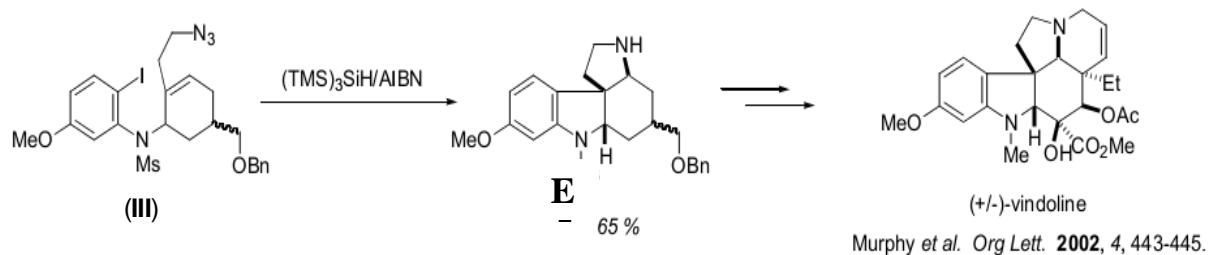


2.2 **D** from the compound (**II**):

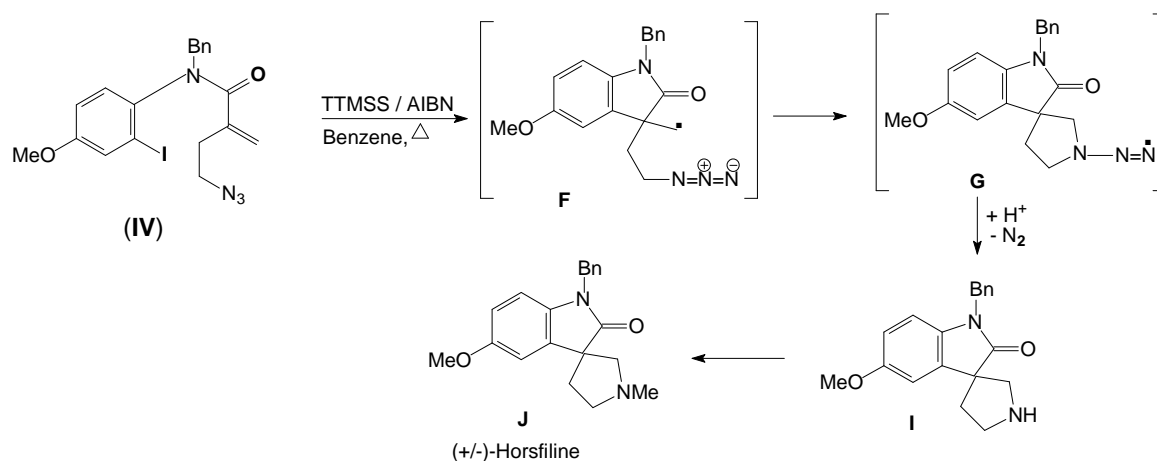




2.3 **E** from the compound **(III)**:

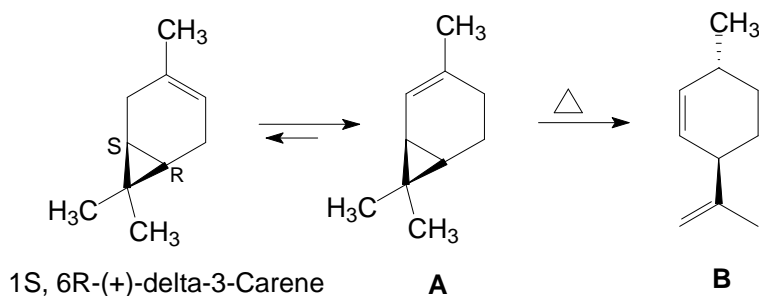


2.4 **I** from the compound **(IV)** through radicals **F** and **G**:

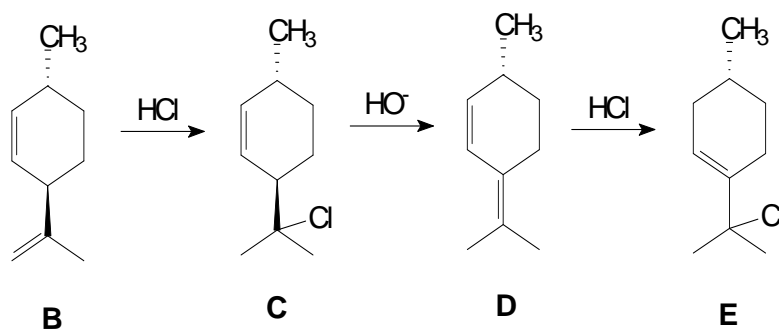


Problem 24. (-)-Menthol from (+)- δ -3-Carene

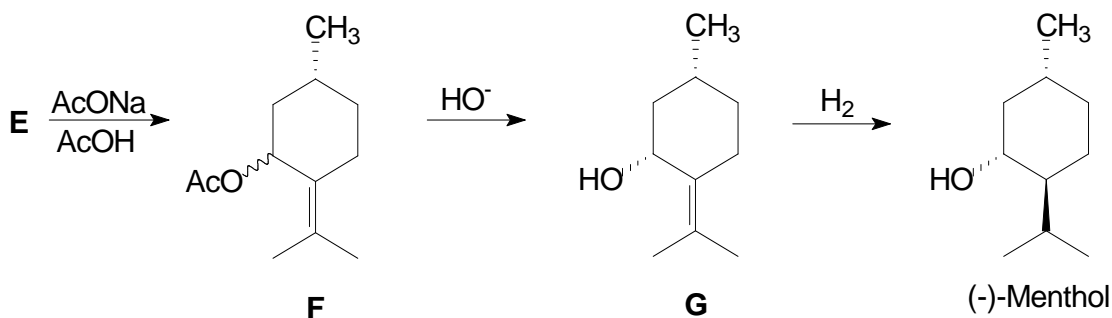
Catalytic isomerisation of δ -3-Carene provides (+)- δ -2-Carene (**A**) which then was pyrolysed to cleave the cyclopropane ring forming diene (**B**):



Treatment of the unconjugated diene (2,8-menthadiene, **B**) with HCl to give **C** and then, dehydrochlorination led to a conjugated diene ((+)-2,4(8)-*p*-menthadiene, **D**). Treatment of (+)-2,4(8)-*p*-menthadiene with hydrogen chloride affords 8-chloro-3-*p*-menthene (**E**):



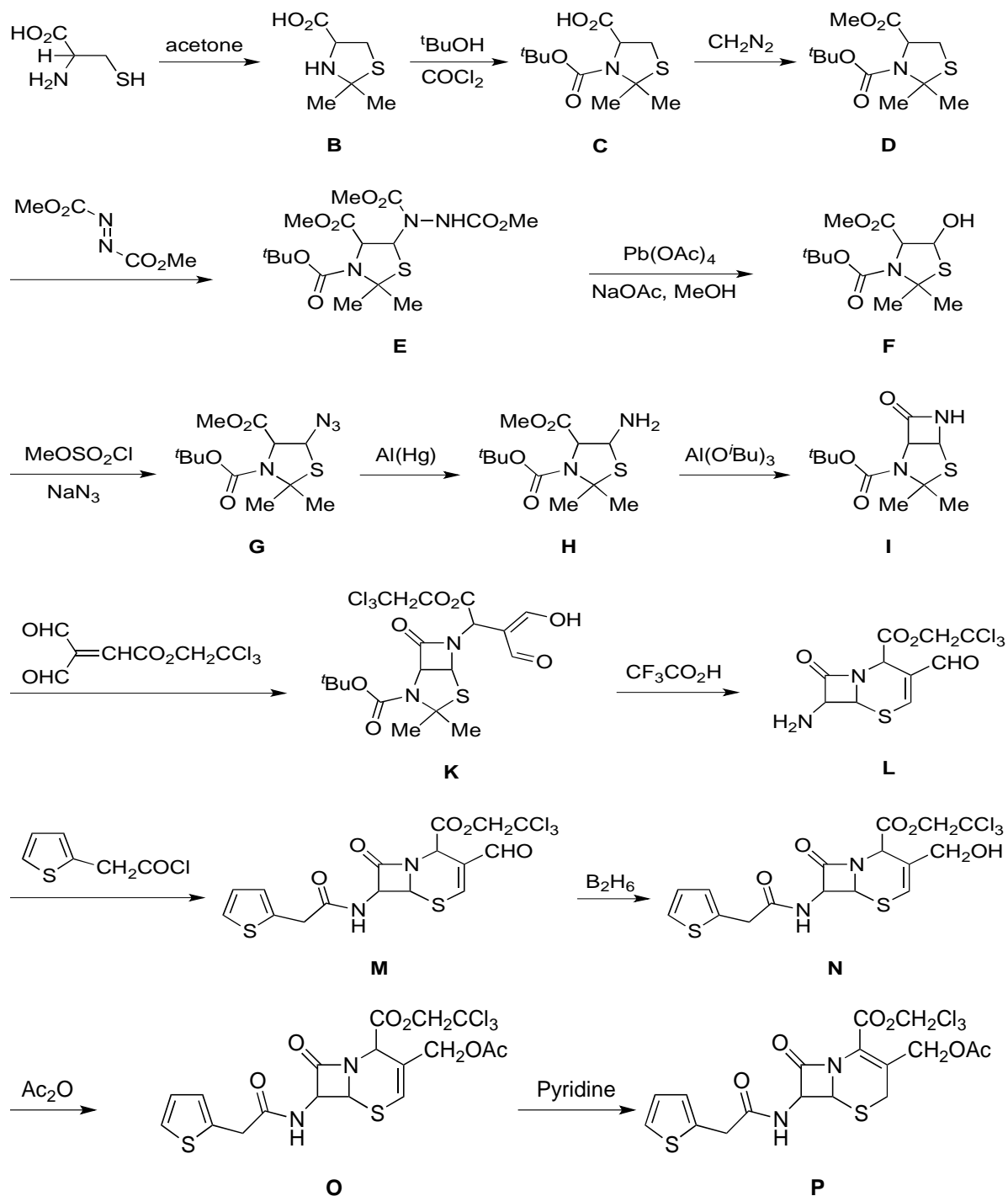
E reacted with sodium acetate and acetic acid to give mixed (*cis/trans*) pulegol esters (**F**) via allylic displacements. Hydrolysis **F** affords (-)-*cis* and (+)-*trans*-pulegol (**G**). Reduction of either pulegol isomer provides menthol isomers which can be readily equilibrated to predominantly (-)-menthol.



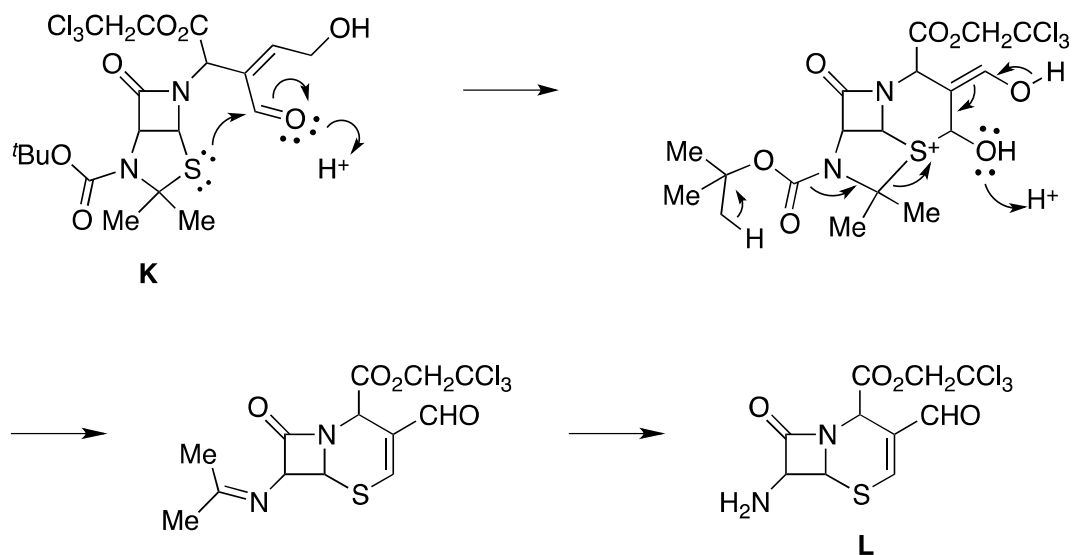


Problem 25. Cefalotin

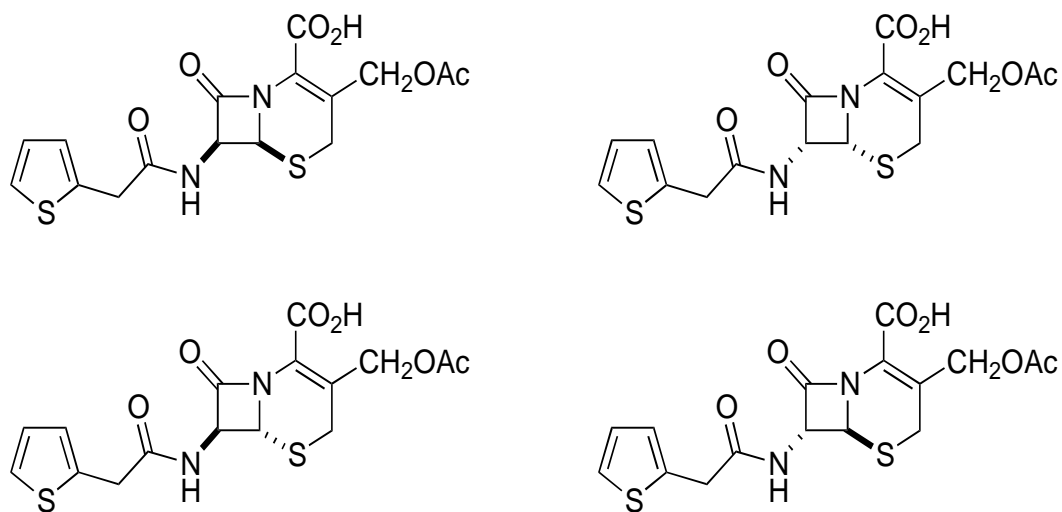
1. Synthetic scheme:



2. Reaction mechanism for the transformation from **K** to **L**



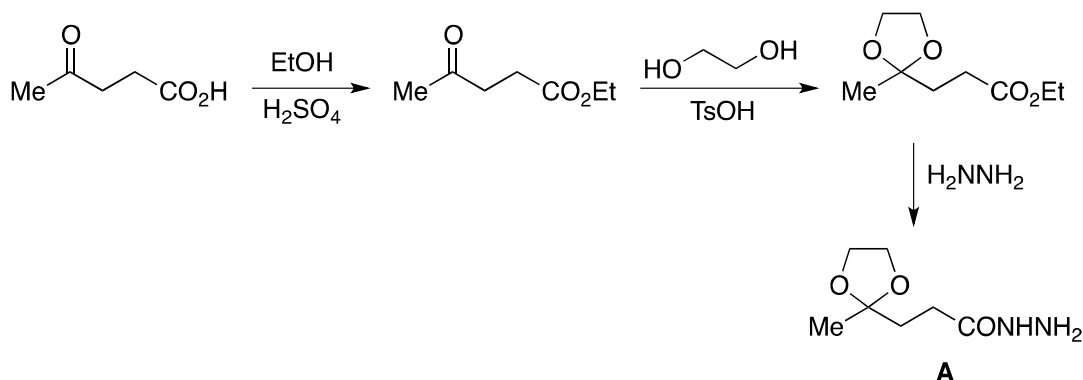
3. There are two asymmetric carbon atoms on cefalotin, so we should expect to have four optical isomers.





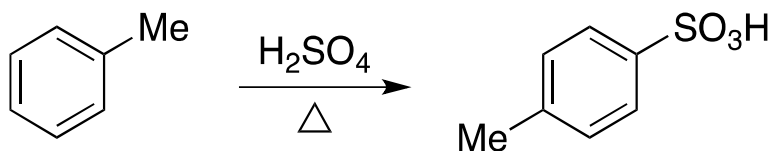
Problem 26. Heterocyclic compounds

1. Synthesis of **A** from levulinic acid:

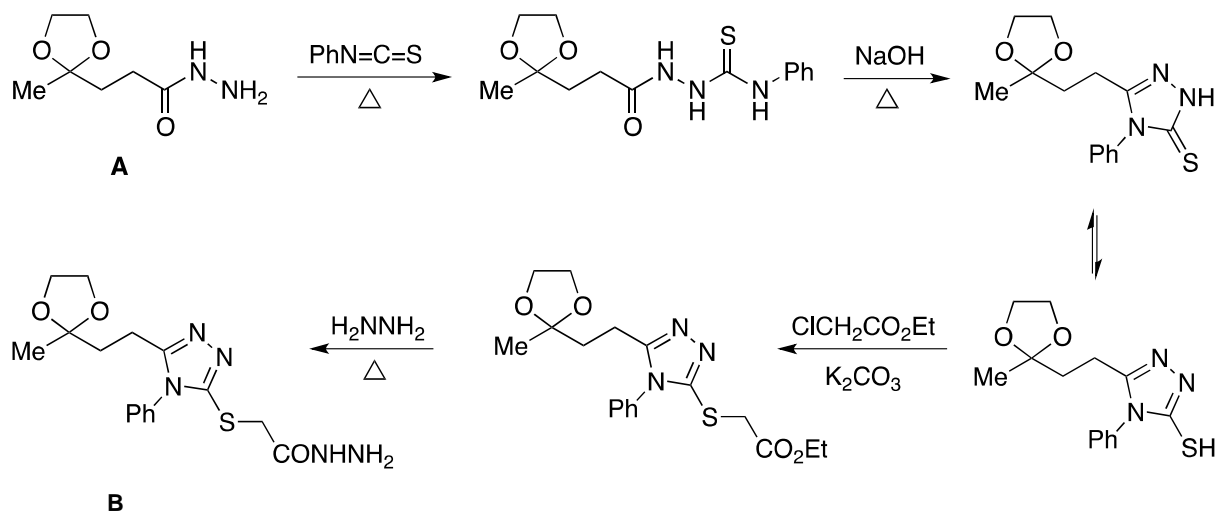


The purpose of 1,3-dioxolane formation was to protect the carbonyl group from the reaction with NH_2NH_2 .

TsOH preparation from toluene:



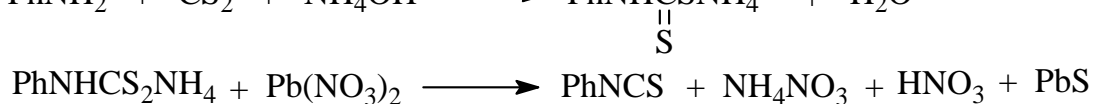
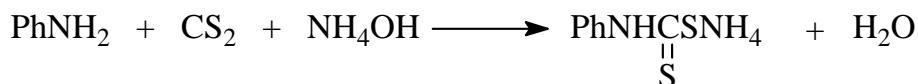
2. Synthesis of **B** from **A**:



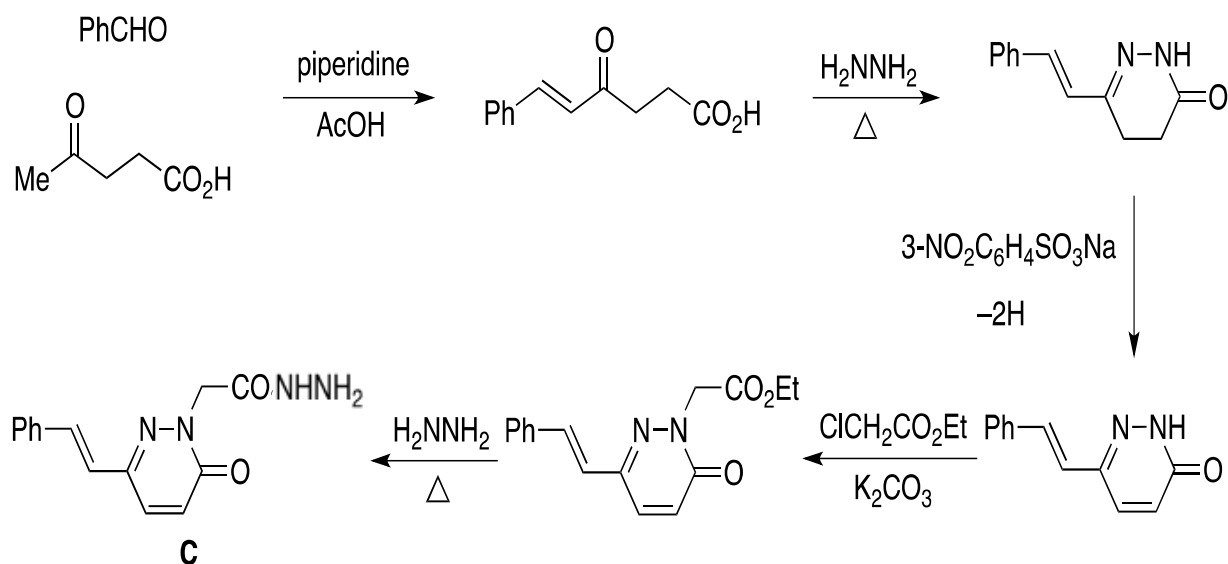


The reaction of **A** and PhNCS is nucleophilic addition of the –NHNH₂ group to the –NCS group.

PhNCS preparation from aniline:

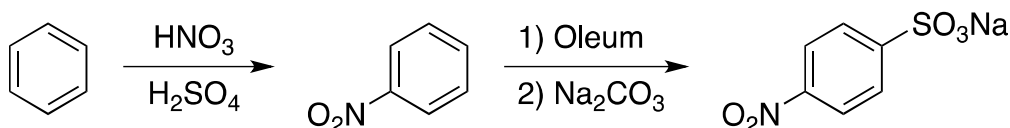


3. Synthesis of **C** from levulinic acid:



3-O₂NC₆H₄SO₃Na is a dehydrogenation (or oxidation) reagent to convert dihydropyridazine into pyridazine ring.

3-O₂NC₆H₄SO₃Na preparation from benzene:



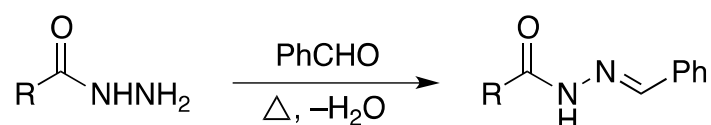
¹H-NMR spectrum:

Before the reaction, the heterocyclic should provide 2 resonance signals with 2H intensity in the strong field of the two CH₂ groups (experimental: 2.57 ppm and

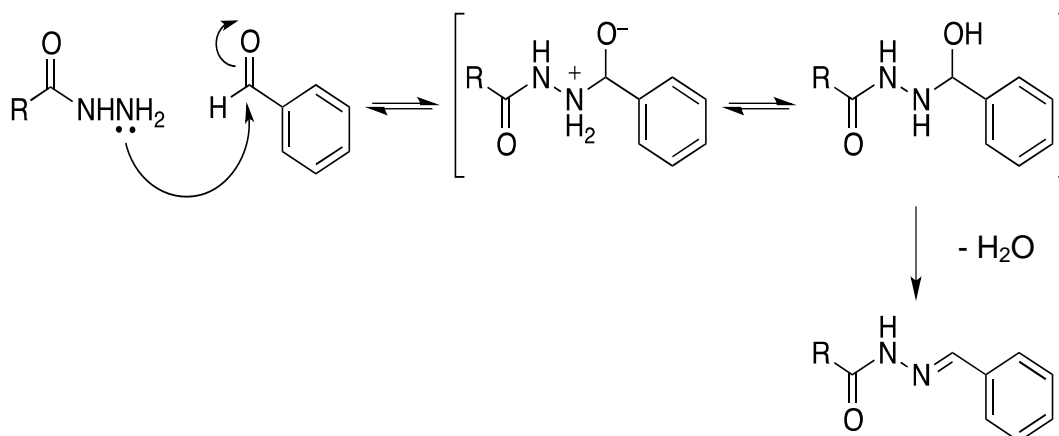


2.83 ppm). After the reaction, these 2 signals should disappear, and two new signals in with 1H intensity the weak field of the two CH groups should appear (experimental: 7.01 ppm and 7.64 ppm).

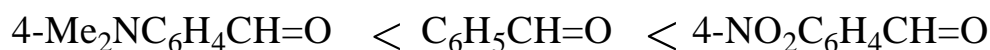
4. Reaction mechanism of R-CONHNH₂ with PhCHO:



First, the hydrazide -CONHNH₂ group performed nucleophilic addition to the C=O group of benzaldehyde, then the dehydration step occurred:



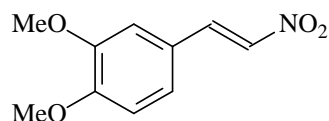
The electron-withdrawing group -NO₂ facilitates the reaction, while the electron-donating group -NMe₂ retards the reaction.



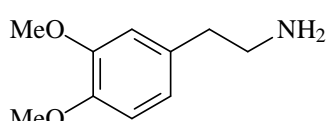


Problem 27. Lotus

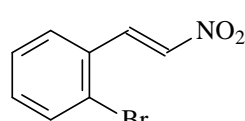
1. Structural formulae and the reaction conditions for (a3) and (b3):



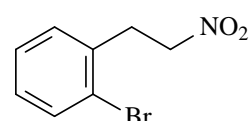
A₁



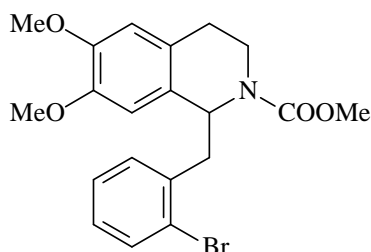
A₂



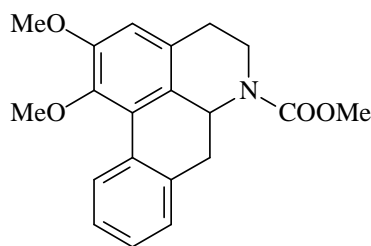
B₁



B₂



X₁



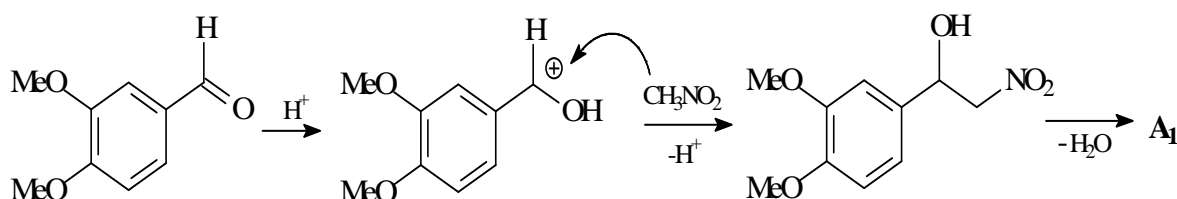
X₂

(a3) MeOCOCl, THF

(b3) 1. NaOH/EtOH 2. H₂SO₄

2. Reaction mechanism:

a. **A₁** from 3,4-dimethoxybenzaldehyde: aldol condensation, the water elimination, (crotonation).

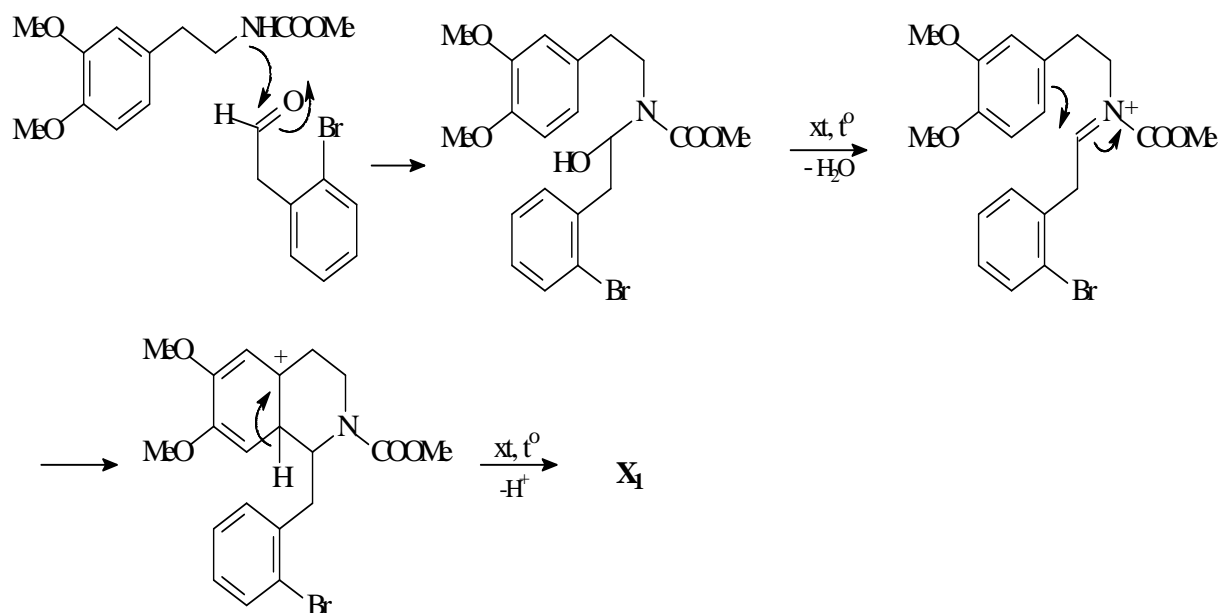


b. Reaction mechanism for the formation of **X₁**: Addition-cyclization as Pictet-Spengler reaction mechanism.

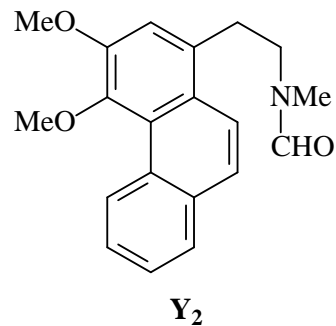
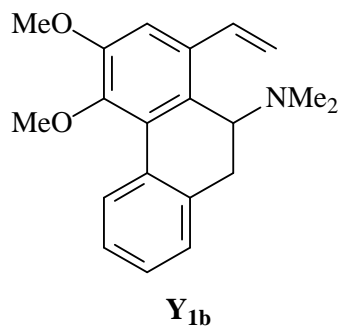
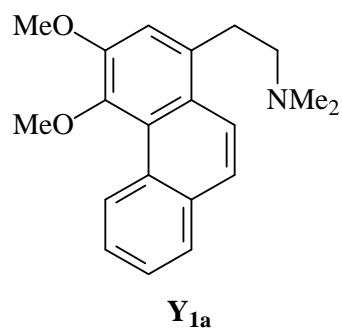


46th International Chemistry Olympiad
Hanoi, Vietnam – 2014

Preparatory Problem
Solutions



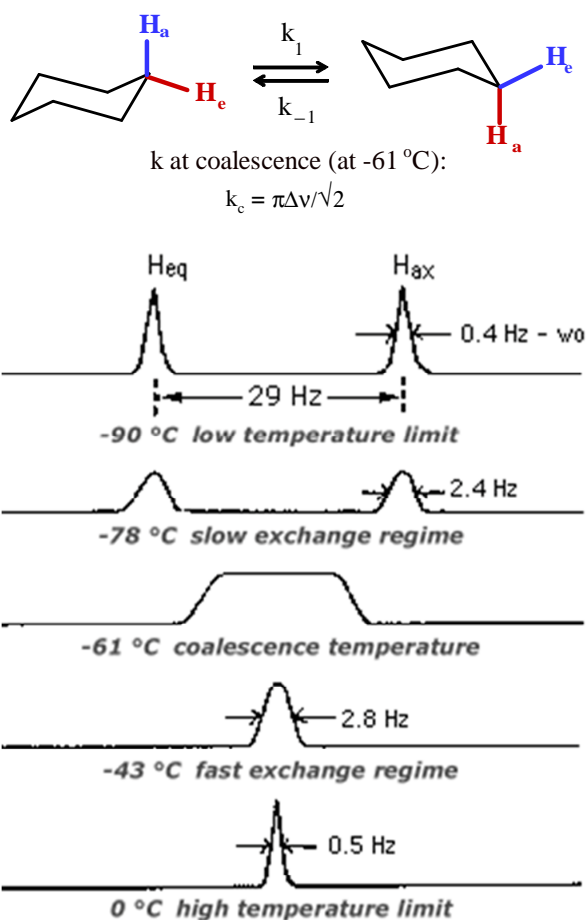
3. Structural formulae for **Y_{1a}**, **Y_{1b}**, **Y₂**:



Problem 28. NMR Spectroscopy

1. A molecule can undergo fluxional process by interchanging two or more sites. If the rate of exchange is faster than the NMR time scale, the two different groups will appear at an average shift. As temperature decreases the rate becomes lower and separate shift can be obtained.

Rapid equilibration at room temperature between chair conformations leads to one peak. As one lowers the temperature, the interconversion is slowed down until, at temperatures below $-66.7\text{ }^{\circ}\text{C}$, peaks due to the axial and equatorial hydrogens are observed. Axial and equatorial hydrogens have different chemical shifts under these conditions.



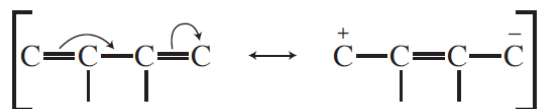


2. The *t*-butyl-substituted rings are conformationally locked. The hydrogen at C1 has different chemical shifts, depending upon whether it is axial or equatorial. 4-Bromocyclohexanes are conformationally mobile. No difference between axial and equatorial hydrogens is observed until the rate of chair–chair interconversion is decreased by lowering the temperature.

Problem 29. Infrared Spectroscopy (IR)

1. Resonance (conjugation) effect: the amino group pushes electron density into the ring and into the carbonyl group resulting in a lower frequency carbonyl group (more single bond character). A nitro group withdraws electrons resulting in higher frequency carbonyl absorption (more double bond character).

2. Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single-bond character (through resonance, as the following example shows), a lower force constant K , and thus a lower frequency of vibration. For example, the vinyl double bond in styrene gives absorption band at 1630 cm^{-1} . Esters show a very strong band for the C=O group that appears in the range of $1750\text{--}1735\text{ cm}^{-1}$ for simple aliphatic esters. The C=O band is shifted to lower frequencies when it is conjugated to a C=C or phenyl group.



(Hint: $\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$, μ : reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$, c : speed of light).



Therefore,

Spectrum A: Methyl acrylate. The absorption band appears at 1726 cm^{-1} belong to the C=O group that conjugates to double carbon-carbon double bond. Similarly, the C=C bond in this molecule has the absorption band at 1639 cm^{-1} due to the stretching vibration.

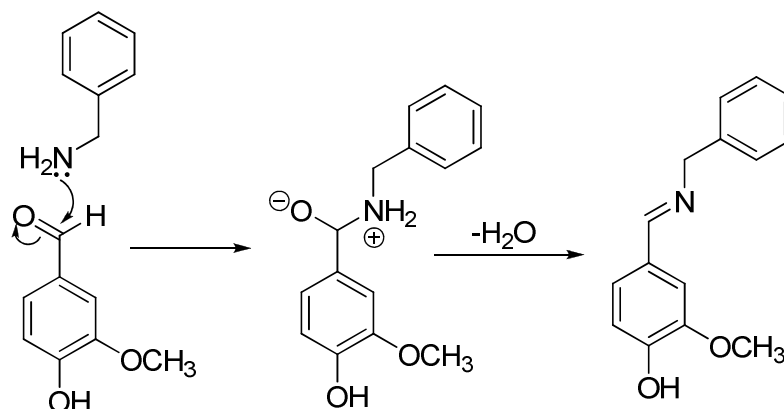
Spectrum B: Allyl acetate. The stretching vibrations of C=O and C=C double bonds appear at the normal positions for these vibrations, at 1743 and 1650 cm^{-1} , respectively.

There are only the separated C=C and C=O double bonds in vinyl propionate and allyl acetate, so the stretching bands appear at the normal positions.

PART 2. PRACTICAL PROBLEMS

Problem 30. Condensation between vanillin and benzylamine

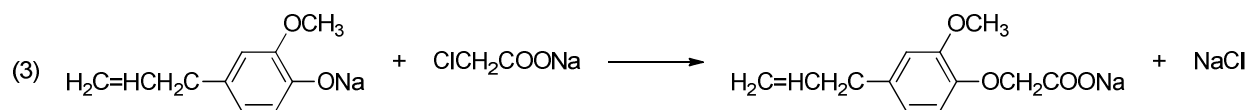
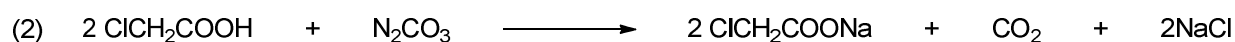
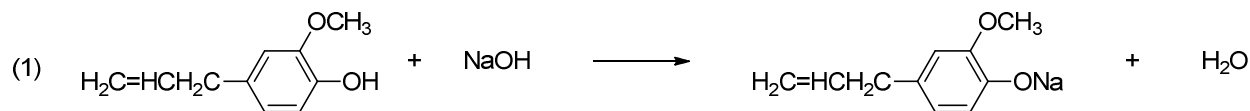
2. Mechanism

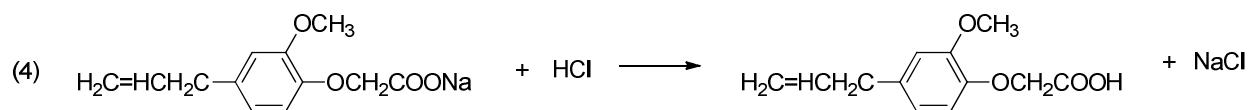


3. Na₂SO₄ is a water-adsorbing substance. It removes water preventing H₂O attack to the product (imine).

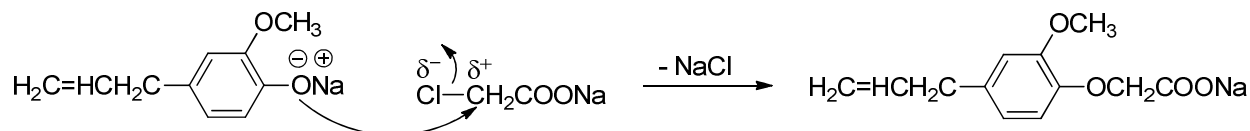
Problem 31. Synthesis of eugenoxo acetic acid

1. Reactions in steps 1a, 1b and 2:



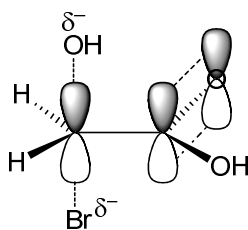


3. The reaction in step 2 follows a S_N2 substitution:



4. In alkaline media, eugenol is transformed into eugenolate which has adequate nucleophilicity to replace the chlorine atom of monochloroacetic acid. An excess amount of alkaline, however, should not be used as the hydroxide ions can compete with the eugenolate ions to form the hydroxide derivative of acetic acid.

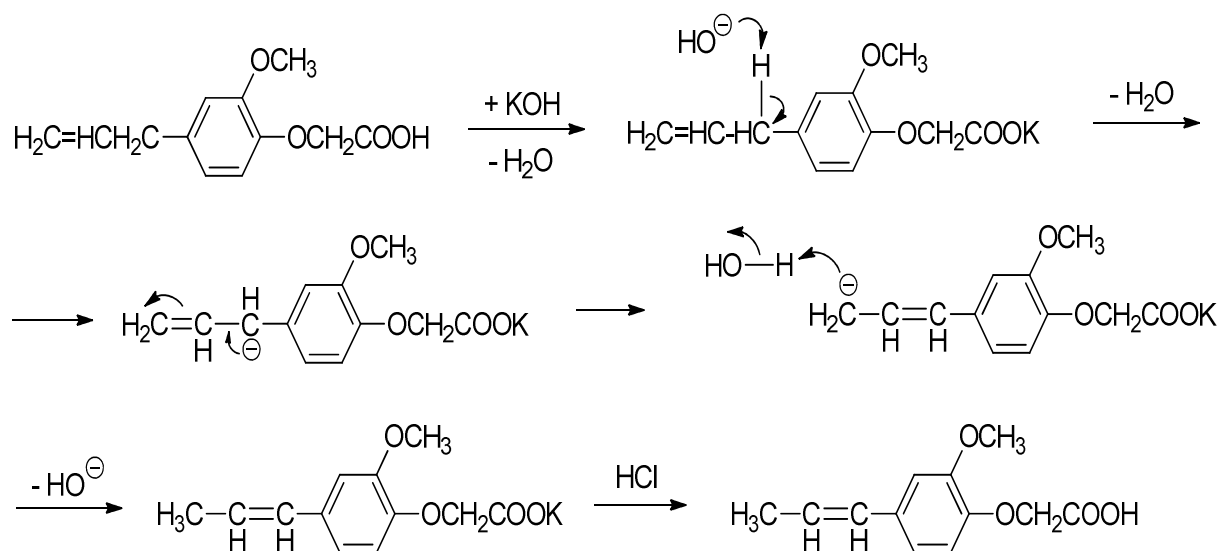
5. The carboxyl group, on the one hand, provides for an (-I) effect to increase the positive charge density at the alpha carbon, facilitating the attack of nucleophiles. On the other hand, the carboxyl can delocalize the negative charges appearing in the transition state of the S_N2 reaction.



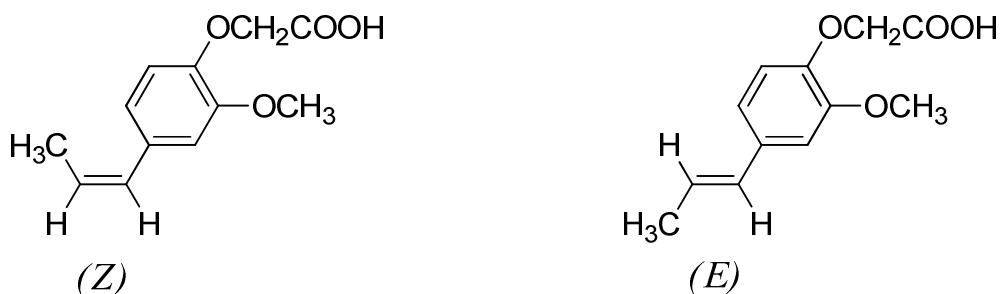
6. Crystallized water in the product re-crystallized from hot water lowers down its melting point. Re-crystallization of the product from dry benzene helps eliminate water and increase the melting point. Titration or TGA can be used to determine the amount of water crystallized in the product



7. In basic condition, eugenoxycetic acid is subjected to isomerization in which the terminal C=C double bond is moved in and conjugated with the benzene ring to yield isoeugenoxycetic acid as shown in the scheme below:



Isoeugenoxycetic acid can exist in form of two configuration isomers (*Z*) and (*E*):



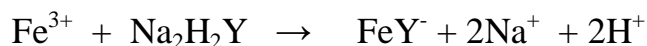


Problem 32. Complexometric titration of iron, aluminum, and magnetism in the aqueous solution

1. The chemical equations of the reactions used in the titration:

1.1 Titration of Fe^{3+}

The stability constant of FeY^- is much larger ($= 10^{25.1}$) \gg The constants of complex of Al^{3+} ($10^{16.13}$) and of Mg^{2+} ($10^{8.7}$) therefore in the solution with pH of 2 only ion Fe^{3+} totally titrated:

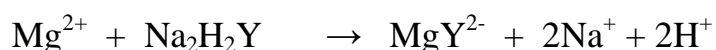


1.2 In the solution with pH of 4.7 only ions Fe^{3+} and Al^{3+} are totally titrated:



1.3 Separate and titration of Mg^{2+} :

In the buffer $\text{NH}_3 + \text{NH}_4^+$ (pH = 9.2) only $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ are precipitated and total Mg^{2+} ions are existed in the solution. After the filtration of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ we can titrate Mg^{2+} in the filtrate:



2. The formulae for calculation of ion concentrations (in mol / L)

$$C_{\text{Fe(III)}} = V_1 \cdot 0.05 / 25.0$$

$$C_{\text{Al(III)}} = [(50.0 - V_2 - V_1) \cdot 0.05] / 25.0$$

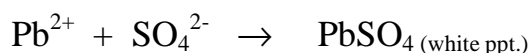
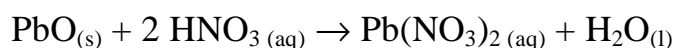
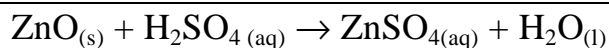
$$C_{\text{Mg(II)}} = V_3 \cdot 0.05 / 25.0$$



Problem 33. Determination of zinc and lead in zinc oxide powder

1.

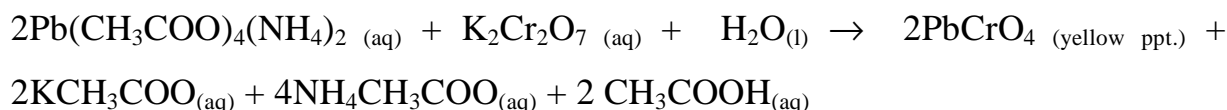
1.1



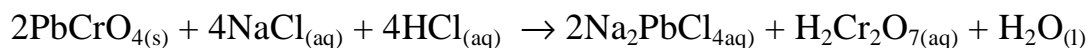
1.2



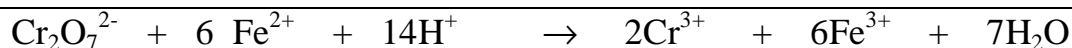
1.3



1.4



1.5



2.

Mass of zinc oxide powder = a (g). The volume of standard solution is recorded in mL.

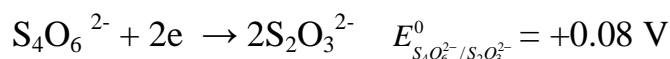
$$\% \text{Zn} = (V_{\text{EDTA}} \times C_{\text{EDTA}}) \times 10 \times 100$$

$$\% \text{Pb} = \frac{1}{3} \times 207.02 \times (V_{\text{Fe}^{2+}} \times C_{\text{Fe}^{2+}}) \times 100$$



3.

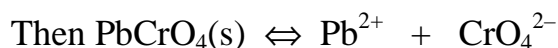
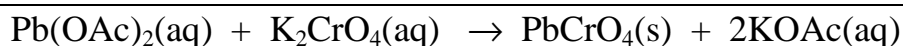
The half reactions $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ $E^\circ = 1.33 \text{ V}$



As $\text{K}_2\text{Cr}_2\text{O}_7$ is a strong oxidant, it can oxidize $\text{S}_2\text{O}_3^{2-}$ to form $\text{S}_4\text{O}_6^{2-}$ and SO_4^{2-} . The reactions are not stoichiometry.

4.

4.1



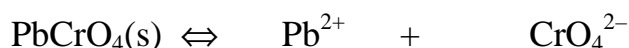
$$[\text{Pb}^{2+}] = 0.1 \times 10^{-5} / 0.12 = 8.3 \times 10^{-6} \text{ mol/L}$$

$$[\text{CrO}_4^{2-}] = 0.02 \times 1.0 \times 10^{-3} / 0.12 = 1.7 \times 10^{-4} \text{ mol/L}$$

Therefore $Q = 8.3 \times 10^{-6} \times 1.7 \times 10^{-4} = 1.4 \times 10^{-9} > K_{\text{sp}}$. So a precipitate will occur.

4.2

Since $[\text{Pb}^{2+}] = 8.3 \times 10^{-6}$ and $[\text{CrO}_4^{2-}] = 1.7 \times 10^{-4}$ and there is a 1:1 stoichiometry, Pb^{2+} is completely reacted.



$$\text{I. (after ppt.)} \quad 8.3 \times 10^{-6} \quad 1.7 \times 10^{-4} - 8.3 \times 10^{-6} = 1.7 \times 10^{-4}$$

$$\text{C.} \quad x \quad x$$

$$\text{E.} \quad x \quad 1.7 \times 10^{-4} + x$$

$$K_{\text{sp}} = [x][1.7 \times 10^{-4} + x] = 1.8 \times 10^{-14}$$

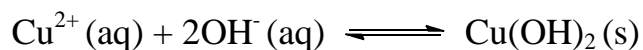
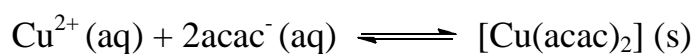
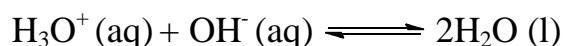
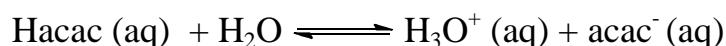
Solving for x gives $x = 1.1 \times 10^{-10}$, so the concentration of Pb^{2+} remaining in solution is very small.



Problem 34. Preparation of copper(II) acetylacetonate

1. $\text{Cu}(\text{acac})_2$

2. There are four main equilibria involved the complex formation:



At a low pH, acac^- is not sufficiently concentrated to precipitate complex or to form the complex with a high yield. On the contrary, at high pH regions, $\text{Cu}(\text{OH})_2$ can be competitively precipitated and an impure product can be obtained.

3. Square planar complex with two six-membered chelate rings.

Problem 35. Kinetic analysis of the hydrolysis of aspirin

1.

The theoretically obtained amount of aspirin is:

$$n_{(\text{salicylic acid})} = 2.00\text{g}/138.1 = 0.0145 \text{ mol}$$

$$m_{(\text{aspirin})} = 0.0145 \text{ mol} \times 180.2 = 2.6129 \text{ g}$$

Experimentally, the amount of aspirin obtained is 2.0132 g

$$\rightarrow \text{The yield of the reaction is: } (2.0132/2.6129) \times 100 = 77.04 \%$$

2. Magnesium hydroxide, magnesium carbonate and aluminum glycinate, when mixed into the formulation of the aspirin will reduce the irritation.

3.

Ignoring the volume change upon mixing and supposing that aspirin occupies only negligible volume:

In the 5×10^{-4} M solution of acetylsalicylic acid, the concentration of NaOH = $(5.0 \times 10^{-3} \text{ mol L}^{-1} \times 40 \text{ mL}) / 50 \text{ mL} - 5.0 \times 10^{-3} \text{ mol L}^{-1} = 3.5 \times 10^{-3} \text{ mol L}^{-1}$

4. Determine the order with respect to the concentration of aspirin and the pseudo - order rate constant of the reaction.

The UV-Vis absorption obtained in the experiments is given below:

Time/minute	5	10	20	30	40	50	60	∞
Absorbance A	0.549	0.829	1.178	1.389	1.506	1.569	1.602	1.653

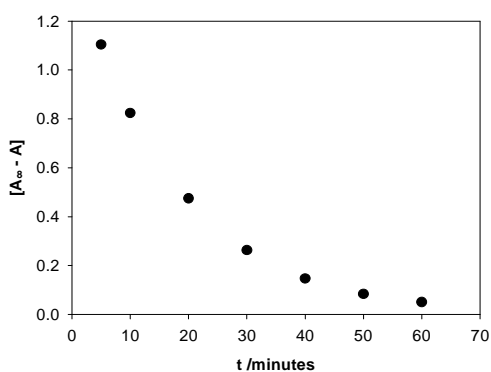


Figure 1. Plot of $(A_{\infty} - A)$ versus time

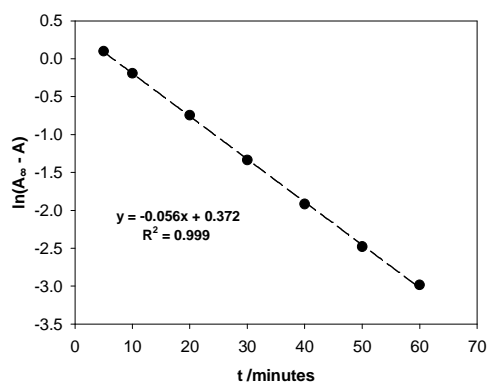


Figure 2. Plot of $\ln(A_{\infty} - A)$ vs. t

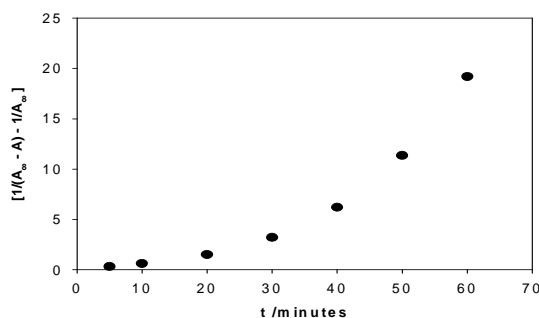


Figure 3. Plot of $\left(\frac{1}{A_{\infty} - A} - \frac{1}{A_{\infty}}\right)$ vs. t

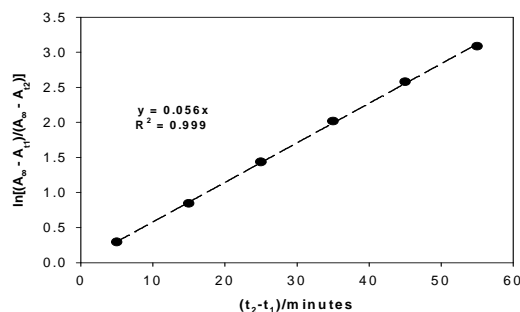


Figure 4. Plot of $\ln \frac{A_{\infty} - A_{t_1}}{A_{\infty} - A_{t_2}}$ vs. $(t_2 - t_1)$

5. Experimental results showed that the reaction obeyed the pseudo-first-order rate law (figure 2 and 4), but not the second-order (figure 3). Based on the equation

$$\ln \frac{A_{\infty} - A_{t_1}}{A_{\infty} - A_{t_2}} = kt \text{ and the results in figure 4, as well as in figure 2, we can easily}$$

calculate $k_{\text{obs}} = 0.056 \text{ min.}^{-1}$. Hence, the half-life is 17.85 minutes and the reaction time is 3.36 times greater than the half-life.

6. From the obtained experimental results the reaction is first order with respect to both $[\text{asp}]$ and $[\text{OH}^-]$, therefore the rate law may be given as

$$\text{Rate} = k [\text{asp}]^1 [\text{OH}^-]^1.$$

According to this mechanism, in step 1, the hydroxide nucleophile attacks at the electrophilic C of the ester $\text{C}=\text{O}$, breaking the σ bond and creating the **tetrahedral intermediate**. In step 2, the intermediate collapses, reforming the $\text{C}=\text{O}$ and, the last step (step 3) is an acid-base reaction which takes place very fast, a very rapid equilibrium. Hence, it is not the rate-determining step of the reaction.

Let denote the **tetrahedral intermediate** as **I** and $(2\text{-HOC}_6\text{H}_4\text{COO}^-)$, a product in step (2) as **P**. The rate of formation of product may be given as



$$\text{Rate} = \frac{d[P]}{dt} = k_2[I]$$

With regard to the stability of the intermediate **I**, the two possibilities, which may be considered, are

i) If $k_{-1} \gg k_2$, means the rate of reconversion of **I** into asp and OH^- is significantly greater than the rate with which it undergoes to give the **P**, the concentration of intermediate **I**, $[I]$ can be calculated by considering equilibrium (1) alone

$$[I] = K[\text{asp}][\text{OH}^-]$$

Where equilibrium constant $K = k_1/k_{-1}$ and, therefore

$$\text{Rate of the reaction} = k_2 K [\text{asp}][\text{OH}^-]$$

which is matching well with experimental results.

ii) If intermediate complex **I** is much less stable species, means the rate of its conversion to product (step 2) is not small compared with the reverse rate in step 1. In this case, the concentration of **I** must be calculated by using steady-state treatment.

By applying the steady state with respect to $[I]$, we get

$$k_1[\text{asp}][\text{OH}^-] = k_{-1}[I] + k_2[I]$$

or

$$[I] = \frac{k_1[\text{asp}][\text{OH}^-]}{k_{-1} + k_2}$$

and, therefore

$$\text{Rate of reaction} = \frac{k_1 k_2 [\text{asp}][\text{OH}^-]}{k_{-1} + k_2}$$

However, when $k_{-1} \gg k_2$, the rate law becomes same as case 1. Thus, the steady state treatment is the general one, and reduces to the equilibrium treatment when $k_{-1} \gg k_2$.

Conclusion: if the equilibrium in step 1 is controlled throughout the reaction process (step 1 is very fast and represents rapid pre-equilibrium to the rate), the



given mechanism agrees with the rate law and in this case the step 2 is rate-determining step of the reaction.

The obtained rate laws clearly show the rate is dependent on the NaOH concentration. For a given concentration of NaOH, we may write

$$\text{Rate of reaction} = k_{\text{obs}} [\text{asp}]$$

$$\text{Where } k_{\text{obs}} = \frac{k_1 k_2 [\text{OH}^-]}{k_{-1} + k_2} \text{ or } k_2 K [\text{OH}^-] \text{ (when } k_{-1} \gg k_2 \text{)}$$

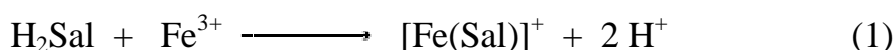
Constant k_{obs} is proportional to $[\text{OH}^-]$ and is known as catalytic coefficient for the catalyst.

Problem 36. Complex formation of ferric ion and salicylic acid

1. $n = 1$, thus the empirical formula is $\text{Fe}^{3+}(\text{H}_2\text{Sal})$

2.

2.1 The chemical equation:



$$\underline{2.2} \quad K_{(1)} = K_f \times K_{a1} \times K_{a2} = \frac{[\text{Fe}(\text{Sal})] \times [\text{H}^+]^2}{[\text{H}_2\text{Sal}] \times [\text{Fe}^{3+}]} \quad \text{or} \quad K_f = \frac{K_{eq} \times [\text{H}^+]^2}{K_{a1} \times K_{a2}}$$

$[\text{H}^+]$ need be calculated from initial concentration 0.0025 M and dissociation concentration during complex formation:

$$[\text{H}^+]_{\text{eq}} = 0.0025 + 2 \times [\text{Fe}(\text{Sal})]^+$$

2.3 The average value is about 1.4×10^{16}



2.4 The average K_f value is not the same with literature values which vary from 2.2×10^{16} to 2.7×10^{16} (ref. 2) due to the simplifications of the equilibrium as mentioned, and also using concentrations instead of activities in the K_f equation.

[1]. D. R. Lide. *CRC Handbook of Chemistry and Physics* (84th Ed). CRC Press, 2003, pp. 1247.

[2] Z. L. Ernst; J. Menashi. *Complex formation between the Fe^{3+} ion and some substituted phenols. Part 1. Spectrophotometric determination of the stability constant of ferric salicylate.* *Trans. Faraday Soc.*, 1963, 59, 1794-1802.

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