49th

International Chemistry Olympiad

PREPARATORY PROBLEMS

Edited by Anton Sirota

33 theoretical problems
5 practical problems

2017

THE PREPARATORY PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Series 4, THE PREPARATORY PROBLEMS FROM THE 49th IChOs

Edited by Anton Sirota

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PREPARATORY PROBLEMS

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THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

Dimerization of Acetic Acid

Ethanoic acid or acetic acid (CH_3COOH) is partially dimerized into dimers in the vapor phase. At a total pressure of 0.200 atm, ethanoic acid is 92.0% dimerized at 298 K. By increasing the temperature to 318 K, the degree of dimerization is lowered, with K_p = 37.3.

1.1 Calculate the enthalpy and the entropy changes for the reaction, assuming that ΔH^o and ΔS^o do not vary with temperature.

1.2 Applying the Le Chatelier's principle, an increase of pressure should (select one correct answer)

◯ favor the dimerization.

◯ not favor the dimerization.

1.3 Continued from question 1.2, the extent of dimerization (select one correct answer)

◯ decreases with increasing the temperature.

◯ increases with increasing the temperature.

_____

SOLUTION OF PREPARATORY PROBLEM 1

1.1 The reaction can be represented as 2 $CH_3COOH \rightleftharpoons (CH_3COOH)_2$.

If we start with, say, 100.0 mol CH_3COOH and 92.0% dimerizes, then 8.0 mol will be present at equilibrium. The 92.0 mol that react give rise to 46.0 mol dimers. The total number of moles present is therefore 54.0. Hence using the data at 298 K, the equilibrium constant, K_p, is given by

$$K_p = \frac{p_{(CH_3COOH)_2}}{p^2_{(CH_3COOH)}} = \frac{x_{(CH_3COOH)_2}\, p_{tot}}{\left(x_{(CH_3COOH)}\, p_{tot}\right)^2} = \frac{\frac{46.0}{54.0} \times 0.200}{\left(\frac{8.0}{54.0} \times 0.200\right)^2} = 194$$

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

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

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

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

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

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

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

Applying the equation $\Delta G^o = \Delta H^o - T\Delta S^o$:

The method for the calculation is to write the two equations

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

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

and solve the equations simultaneously.

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

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

✓ favor the dimerization.

1.3 The extent of dimerization:

✓ decreases with increasing the temperature.

THEORETICAL PROBLEM 2

Solubility of Calcite

Calcite is a stable form of calcium carbonate ($CaCO_3$). The solubility product (K_{sp}) is decreased with increasing temperature; K_{sp} are 9.50×10^{-9} and 2.30×10^{-9} at 0 °C and 50 °C, respectively. Estimate the enthalpy change for the solubility process of calcite.

_____

SOLUTION OF PREPARATORY PROBLEM 2

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

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

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

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

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

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

THEORETICAL PROBLEM 3

Expansion of Ideal Gas and Thermodynamics of Liquid Mixing

3.1 A quantity of 0.10 mol of an ideal gas **A** initially at 22.2 ^{o}C is expanded from 0.200 dm^3 to 2.42 dm^3. Calculate the values of work (w), heat (q), internal energy change (ΔU), entropy change of the system (ΔS_{sys}), entropy change of the surroundings (ΔS_{surr}), and total entropy change (ΔS_{univ}) if the process is carried out isothermally and irreversibly against an external pressure of 1.00 atm.

3.2 If 3.00 mol of **A** is condensed into liquid state and is mixed with 5.00 mol of liquid **B**, calculate the changes in entropy and Gibbs free energy upon such mixing at 25.0 °C. This mixture can be assumed to be ideal.

_____

SOLUTION OF PREPARATORY PROBLEM 3

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

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

$= -225 \text{ J}$

$q = 225 \text{ J}$

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

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

$= 2.07 \text{ J K}^{-1}$

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

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

The other functions are given by these equations:

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

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

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

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

$= -1639 \text{ J mol}^{-1}$

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

THEORETICAL PROBLEM 4

Vibrational Frequency of a Diatomic Molecule

For the vibrational motion of a diatomic molecule using a harmonic oscillator model, the allowed vibrational energy levels can be described as

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right) h\nu \quad ; \upsilon = 0, 1, 2, ...$$

where υ is the vibrational quantum number and ν is the vibrational frequency. The vibrational frequency represented by the harmonic oscillator model is

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, where k is the force constant and μ is the reduced mass.

For molecule CX, where X is an unknown atom, the vibrational absorption energy from vibrational ground state to the first vibrational excited state is 2170.0 cm^{-1} and the force constant is 1.903×10^3 kg s^{-2}.

4.1 Find the reduced mass of CX in amu.

4.2 What is atom X?

SOLUTION OF PREPARATORY PROBLEM 4

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

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

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

$\Delta E = E_1 - E_o = h\nu$

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

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

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

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

$$\mu = \frac{1.903 \times 10^3}{4 \times 3.14^2 \times (2.9979 \times 10^{10}\ \text{cm s}^{-1})^2 (2170.0\ \text{cm}^{-1})^2}$$

$$\mu = 1.140 \times 10^{-26}\ \text{kg} = 6.866\ \text{amu}$$

4.2 To find mass of the atom X, m_x:

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

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

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

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

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

$$m_X = \frac{6.866 \times 12.011}{12.011 - 6.866} = \frac{82.47}{5.145} = 16.03$$

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

THEORETICAL PROBLEM 5

Water-gas-shift Reaction

In a drive toward cleaner energy production, fuel cell holds great promise because of its capability of generating electricity directly from chemical reactions with environmentally-benign byproducts. In particular, for hydrogen fuel cell, the only waste produced by the device is just water.

In order to use fuel cell at an industrial scale, continuous production of hydrogen that directly feeds into a fuel cell module is required. One option to mass produce hydrogen for this purpose is the conversion of hydrocarbon fuel using hot steam. However, this kind of reaction often leads to mixed products that consist of H_2, CO_2, and CO. Moreover, CO is not only hazardous to human health, but it also degrades fuel cell's active material. The reversible water-gas-shift (WGS) reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$, provides one method of converting toxic CO into CO_2 and useful H_2. The efficiency of this reaction strongly depends on the solid catalyst used.

5.1 In one process, an equimolar mixture of CO and steam is continuously passed to a WGS reactor containing catalyst at atmospheric pressure and 0 °C. Assuming that the catalyst is 95.0% efficient in converting the reactants into the products and that the reaction in the reactor is approximately at equilibrium in this condition, estimate the free energy change for this reaction?

5.2 Now assume that a large surface of catalyst is initially available to reacting molecules, and the rate of reaction is measured immediately at the onset of the reaction. Below are the initial rates measured at different initial pressures of CO and H_2O.

Trial	p(CO), atm	$p(H_2O)$, atm	$dp(H_2)/dt$, atm s^{-1}
1	0.10	0.90	4.0×10^{-4}
2	0.15	0.85	5.6×10^{-4}
3	0.25	0.75	8.2×10^{-4}
4	0.28	0.72	X

What is X?

5.3 In another condition where the pressure of hydrogen is found to be 0.50 atm, $-d\mathrm{p}(H_2)/dt = 3.0\times10^{-7}$ atm s^{-1}. According to the information given in questions 5.1, 5.2, and this question, estimate the rate of hydrogen production when the pressures in the reactor of CO, H_2O, CO_2, and H_2 are 0.14, 0.14, 0.36, and 0.36 atm, respectively. (Give your answer to three significant figures.)

5.4 Calculate the Gibbs free energy change for the conditions described in question 5.3.

5.5 Surface coverage, θ, is an important kinetics parameter, especially for reactions on solid surfaces. It can be defined as the number of adsorbed molecules on a surface divided by the total number of adsorbing sites on that surface. For WGS, after the adsorption of CO and H_2O on the catalyst's surface, a carbonyl intermediate can be formed, which then dissociates to give surface-bound CO_2 and H atom. If the carbon dioxide is produced at a rate of 1.0×10^{11} molecules s^{-1} cm^{-2} with associated rate constant of 2.0×10^{12} molecules $s^{-1}cm^{-2}$, what is the value of θ for this intermediate?

SOLUTION OF PREPARATORY PROBLEM 5

5.1 The mole fraction of H_2 in the reactor,

$$x_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{CO_2} + n_{H_2O} + n_{CO}} = \frac{0.475}{1.0} = 0.475$$

Thus,

$p_{H_2} = x_{H_2}\, p_{total} = 0.475 \times 1.00 \text{ atm} = 0.475 \text{ atm}$

And likewise, $p_{CO2} = 0.475$ atm and $p_{H2O} = p_{CO} = 0.025$ atm

$$K = \frac{p_{H_2}\, p_{CO_2}}{p_{H_2O}\, p_{CO}} = \frac{0.475 \times 0.475}{0.025 \times 0.025} = 3.6 \times 10^2$$

Therefore,

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

5.2 The kinetics data given reflects the forward rate of the WGS reaction. The only rate law that is consistent with the given data is $r_f = k_f\, p_{CO}\, p_{H2O}$, and k_f = 4.4 × 10^{-3} atm^{-1} s^{-1}. Thus, X = (4.4 × 10^{-3} atm^{-1} s^{-1})(0.28 atm)(0.72 atm) = 8.9 × 10^{-4} atm s^{-1}.

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

So during the normal course of the reaction,

$r = r_f - r_b = k_f p_{CO} p_{H_2O} - k_b p_{CO_2} p_{H_2} =$

(4.4×10^{-3} atm^{-1}s^{-1})(0.14 atm)(0.14 atm) – (1.2×10^{-5} atm^{-1}s^{-1})(0.36 atm)(0.36 atm) =

= 8.44 × 10^{-5} atm s^{-1}.

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

– 9.1 kJ mol^{-1}

5.5 The reaction $CO_2H(ads) \rightarrow CO_2(ads) + H(ads)$ is first-order, whose rate can be expressed as rate = k[CO_2H] = kθS_0 = k′θ, where S_0 denotes the maximum number of adsorbed intermediates for this surface.

Thus, θ = rate/k′ = (1.0 × 10^{11} molecules s^{-1} cm^{-2}) / (2.0 × 10^{12} molecules s^{-1} cm^{-2}) =

= 0.050.

THEORETICAL PROBLEM 6

Camphor in Benzene

The vapor pressure of pure benzene (C_6H_6) is 100 torr at 26.1 ^oC. Calculate the vapor pressure and the freezing point of a solution containing 24.6 g of camphor ($C_{10}H_{16}O$) dissolved in 100 cm^3 of benzene. The density of benzene is 0.877 g cm^{-3}. The freezing point and the cryoscopic constant (K_f) of pure benzene are 5.50 ^oC and 5.12 ^oC kg mol^{-1}, respectively.

_____

SOLUTION OF PREPARATORY PROBLEM 6

$x_{ben} = n_{ben} / (n_{ben} + n_{cam})$

n_{ben} = 100 cm^3 × 0.877 g cm^{-3} × (1 mol / 78.1 g) = 1.12 mol

n_{cam} = 24.6 g × (1 mol / 152.2 g) = 0.162 mol

x_{ben} = 1.12 mol / (1.12 mol + 0.162 mol) = 0.874

$p_{ben} = x_{ben}\ p^o_{ben}$ = 0.874 ×100 torr = 87.4 torr

m_{ben} = 100 cm^3 × 0.877 g cm^{-3} × (1 kg/1000 g) = 0.0877 kg

molality of camphor in solution = 0.162 mol camphor / 0.0877 kg benzene = 1.85 mol kg^{-1}

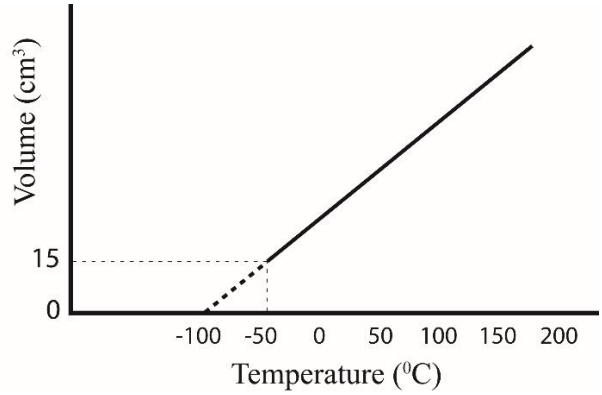
$\Delta T = K_f$ m = 5.12 ^oC kg mol^{-1} × 1.85 mol kg^{-1} = 9.46 ^oC

Since pure benzene freezes at 5.50 ^oC, the solution will freeze at –3.96 ^oC.

THEORETICAL PROBLEM 7

Gas and Liquid

At temperatures above the boiling point, **A** behaves like an ideal gas. In a hypothetical situation, Jacques Charles performed an experiment about the volume-temperature relationship and obtained the following result (which is not necessarily drawn to scale):



7.1 What is the volume of **A** at 100 ^{o}C?

7.2 At equilibrium, the vapor pressures above liquids **B** and **C** are 100.1 kPa and 60.4 kPa, respectively. The two liquids **B** and **C** are mixed thoroughly at 298 K. What is the vapor pressure above a mixture containing 3 mol **B** and 4 mol **C**?

7.3 What are the mole fractions of **B** and **C** above the mixture explained in question 7.2?

_____

SOLUTION OF PREPARATORY PROBLEM 7

7.1 According to the graph, the volume becomes zero at T = –100 ^{o}C. This means that the absolute temperature should be calculated as T(K) = ^{o}C + 100 (not T (K) = ^{o}C + 273.15).

If V_1 = 15 cm^3, T_1 = – 50 ^{o}C + 100 = 50 K, and T_2 = 100 ^{o}C + 100 = 200 K, then we have (15 cm^3 / 50 K) = (V_2 / 200 K).

Therefore, V_2 = (15 cm^3 × 200 K) / (50 K) = 60 cm^3.

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

$p_{total} = p_B + p_C$ (1)

Using the Raoult's law, the total pressure may be obtained by substituting each p term with

$p_i^{\circ} \times x_i$, where p_i° is vapor pressure above pure liquid i and x_i is mole fraction of liquid i:

$p_{total} = (p_B^{\circ} x_B) + (p_C^{\circ} x_C)$ (2)

We know from the question that there are 7 mol of liquid. We obtain the respective mole fractions x: the mole fraction of **B** is 3/7 and the mole fraction of **C** is 4/7.

Substituting values of x_i and p_i° into equation (2) yields the total pressure P_{total} as follows:

p_{total} = (100.1 kPa × 3/7) + (60.4 kPa × 4/7) = 42.9 kPa + 34.5 kPa = 77.4 kPa

7.3 From the definition of mole fraction X, we say

$$x_{vapor\ B} = \frac{moles\ of\ B\ in\ the\ vapor}{total\ number\ of\ moles\ in\ the\ vapor\ phase}$$

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

$$x_{vapor\ B} = \frac{pressure\ of\ B}{total\ pressure}$$

Substituting numbers from question 7.2:

$x_{\text{vapor B}}$ = 42.9 kPa / 77.4 kPa = 0.554

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

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

THEORETICAL PROBLEM 8

Decomposition of Nitrous Oxide

Nitrous oxide decomposes exothermically into nitrogen and oxygen, at a temperature of approximately 565 °C.

$$2\ N_2O \rightarrow 2\ N_2(g) + O_2(g)$$

This reaction follows the second-order kinetics when carried out entirely in the gas phase.

8.1 If the reaction is initiated with $[N_2O]$ equal to 0.108 mol dm^{-3}, what will its concentration be after 1250 s have elapsed at 565 °C? The rate constant for the second order decomposition of N_2O is 1.10×10^{-3} dm^3 mol^{-1} s^{-1} at this temperature.

8.2 The activation energy for the second order reaction at 565 °C is 234 kJ mol^{-1}. What is the rate constant for the reaction at 600 ^oC?

SOLUTION OF PREPARATORY PROBLEM 8

8.1 Because the reaction is second order, therefore

$$\frac{1}{[N_2O]_t} - \frac{1}{0.108\ mol\ dm^{-3}} = (1.10\times10^{-3}\ dm^3\ mol^{-1}\ s^{-1})(1250\ s)$$

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

8.2 Using Arrhenius equation,

$$\ln\frac{k_2}{1.10\times10^{-3}\ dm^3\ mol^{-1}\ s^{-1}} = -\frac{234\times10^3\ J\ mol^{-1}}{8.314\ J\ mol^{-1}\ K^{-1}}\left[\frac{1}{873\ K} - \frac{1}{838\ K}\right]$$

$k_2 = 4.23\times10^{-3}$ dm^3 mol^{-1} s^{-1}

THEORETICAL PROBLEM 9

Avogadro's Number

An internationally accepted procedure is as follows:

We start with a "perfect" sphere of pure ^{28}Si isotope. The mass of this sphere is W g. The volume *V* of the sphere is found from the accurate measurement of the diameter of the sphere. The unit cell of a crystal of silicon is a "diamond cubic lattice", *i.e.* a face-centered unit cell but with 4 Si atoms inside the cube. The length of the unit cell can be determined precisely from X-ray crystallographic measurements of a single crystal of ^{28}Si isotope.

The experimental data are as follow:

Mass of the sphere, W: 1000.064 543(15) g

Volume of the sphere: 431.049 110(10) cm^3

Length of the unit cell, α: 543.099 619(20) pm

Atomic mass of ^{28}Si, M(Si) = 27.976 970 029(23) g mol^{-1}

Number of Si atoms in the unit cell, *N*.

9.1 Write down the equation for calculating Avogadro's number N_A in terms of the parameters.

9.2 How many silicon atoms are in the unit cell?

9.3 Calculate Avogadro's number using the above data. Give answer to 7 significant figures.

SOLUTION OF PREPARATORY PROBLEM 9

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

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

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

The amount of substance of Si in the sphere: $n(\text{Si}) = (W/A)$ (W is mass of the sphere)

The number of silicon atoms in sphere = $n(\text{Si}) \times N_A$.

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

$N_A = n(V/v) \times (\text{A/W})$

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

n = 8

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

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

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

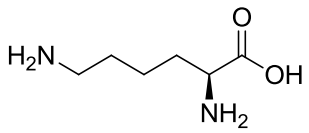
THEORETICAL PROBLEM 10

Buffer from Biological Acid: Lysine

10.1 Acid Dissociation Constants

Name	Carboxylic acid pK_a	Ammonium pK_a	Substituent pK_a
Lysine	2.16	9.06	10.54

One of essential amino acids, lysine, is normally depicted using the molecular structure below: Note that the amine group on the left is part of the substituent group. Is lysine likely to exist in this form when dissolved in neutral aqueous solution? If not, write the correct form.



10.2 Draw the molecular structures for dominant forms of lysine that are present in aqueous solution and arrange them in order from the most acidic form to the most basic form. Use Na^+ or Cl^- to balance the charge. Label each structure with the name of the compound.

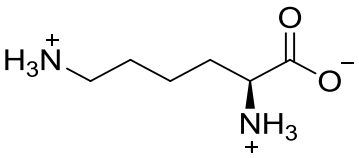
10.3 To prepare buffer solution, you start with the most acidic form of lysine that has the concentration of 0.100 mol dm^{-3} with the volume of 100 cm^3. Calculate the volume of KOH solution with a concentration of 0.500 mol dm^{-3} you should add to obtain a pH of 9.5?

10.4 Dissolve 5.00 g of the neutral zwitterion form of lysine in 100.0 cm^3 of pure water. Determine pH of the solution once equilibrium is reached.

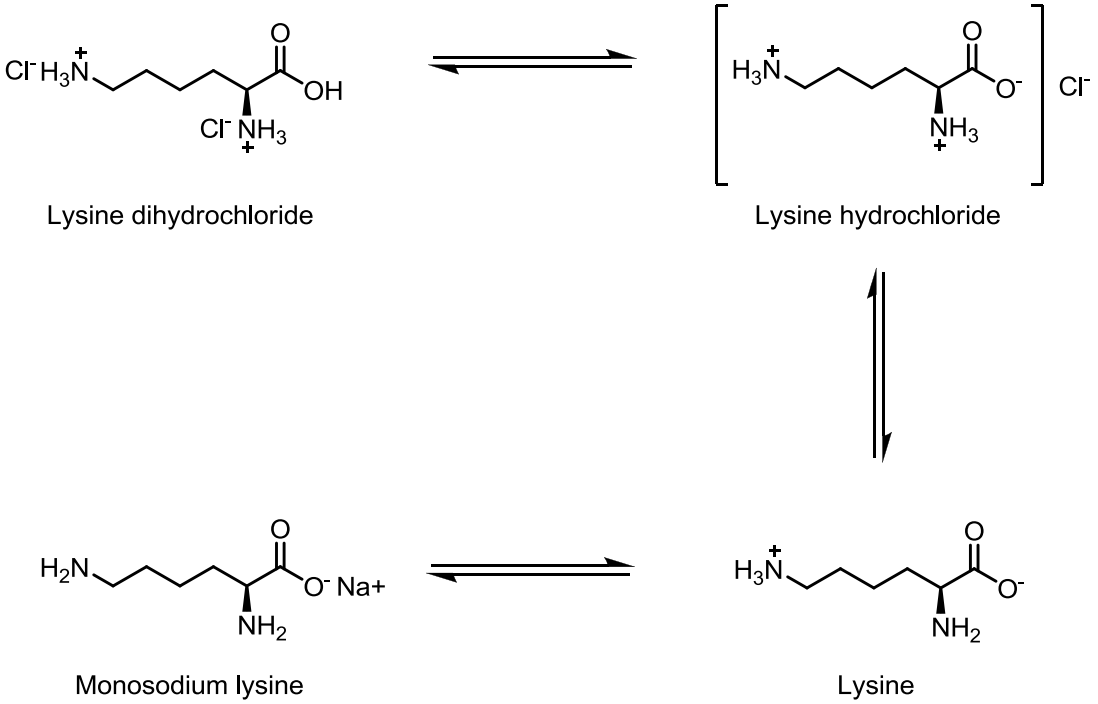
10.5 Determine the equilibrium concentrations of all other forms of lysine present in the solution prepared in question 10.4.

SOLUTION OF PREPARATORY PROBLEM 10

10.1 No. The correct form is as shown:



10.2



10.3 Let us mark: H_3L^{2+} - the most acidic form

H_2L^{+} - the first intermediate form

HL - the second intermediate form

L^{-} - the most basic form

$c(H_3L^{2+}) = [H_3L^{2+}] + [H_2L^{+}] + [HL] + [L^{-}] = 0.1$ mol dm^{-3}

total $n(H_3L^{2+}) = (0.100 \text{ mol dm}^{-3})(0.1 \text{ dm}^3) = 0.01$ mol

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

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

At pH = 9.5, the equilibrium amount of substances of all forms can be calculated as follows:

$$n(H_3L^{2+}) = \textit{total } n(H_3L^{2+}) \frac{[H^+]^3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} = 1.14 \times 10^{-3} \text{ mol}$$

(negligible)

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

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

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

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

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

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

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

1 mol of KOH required = $(2.497\times10^{-3}) + 2(6.88\times10^{-3}) + 3(6.27\times10^{-4})$

$= 1.814\times10^{-2}$ mol

1 cm^3 of KOH solution required = (1000 cm^3 / 0.5 mol) 1.813×10^{-2} mol = 36.28 cm^3

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

HL is the second intermediate form

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

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

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

[HL] = 0.342

$$[H^+] = \sqrt{\frac{[10^{-9.06}10^{-10.54}(0.342)] + [10^{-9.06}10^{-14})}{10^{-9.06} + 0.342}} = 1.59\times10^{-10}$$

pH = 9.80

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

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

$HL + H_2O \leftrightarrows H_2L^+ + OH^-$ $\quad K_{b2} = K_w / K_{a2} = 1\times10^{-14} / 1\times10^{-9.06} = 1.15\times10^{-5}$

From question 10.4: $[H^+] = 1.59\times10^{-10}$

Then $[OH^-] = 6.29\times10^{-5}$

At equilibrium:

$$[HL] = c_{HL}\frac{K_1 K_2 [H^+]}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}$$

Where: $c_r(HL) = 0.342$

$[HL] = 0.250$

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

$$[L^-] = \frac{K_{a3}[HL]}{[H^+]} = \frac{10^{-10.54}\times 0.250}{1.59\times10^{-10}} = 0.0453$$

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

$$[H_2L^+] = \frac{K_{b2}[HL]}{[OH^-]} = \frac{1.15\times10^{-5}\times 0.25}{6.29\times10^{-5}} = 0.0457$$

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

$$K_{b3} = \frac{K_w}{K_{a1}} = \frac{10^{-14}}{10^{-2.16}} = 1.45\times10^{-12}$$

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

$$[H_3L^{2+}] = \frac{K_{b3}[H_2L^+]}{[OH^-]} = \frac{1.45\times10^{-12}\times0.0457}{6.29\times10^{-5}} = 1.05\times10^{-9}$$

THEORETICAL PROBLEM 11

Amperometric titration: Titration of Pb^{2+} with $Cr_2O_7^{2-}$

Amperometry is one of the sensitive electroanalytical methods used for quantitative determination of electroactive species. A working electrode is held at a certain voltage (*vs* reference electrode) that is suitable for oxidation or reduction of an analyte. The analyte will be oxidized or reduced at the surface of the working electrode and the current passing through this electrode is measured. This current is directly proportional to the concentration of analyte and is used for quantitative purpose. It can be used for detection of titration end-point. In this example amperometric detection was used for monitoring a titration progress. A volume of 20 cm^3 of a lead (II) ion solution was titrated with 0.0020 mol dm^{-3} potassium dichromate solution. A dropping mercury electrode (DME) was used as a working electrode and the potential of -0.8 V (*vs* SCE, saturated calomel electrode) was applied to this electrode for enabling the reduction of lead (II) ion and dichromate ion with potassium nitrate as supporting electrolyte. The current-volume of titrant data are shown in Table 1.

Reference: Vogel's Textbook of Quantitative Chemical Analysis, 5th edition, John Wiley & Sons, New York, pp630.

Table 1. Titration data

Volume (cm^3) of 0.0020 mol dm^{-3} dichromate	Current (microampere)
0.00	9.8
2.00	8.0
4.00	6.0
6.00	4.0
8.00	2.2
10.00	3.5
12.00	5.5
14.00	7.6
16.00	9.5

11.1 Plot the titration curve and find the titration end point. (The point where the change in the slope of titration curve occurs)

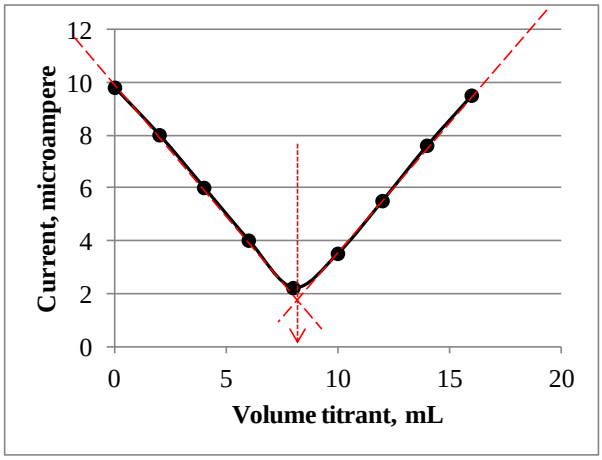
11.2 Write the titration reaction.

11.3 Calculate the concentration of lead(II) cations.

_____

SOLUTION OF PREPARATORY PROBLEM 11

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



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

11.3 $n(Pb^{2+}) = n(\text{dichromate})$

$0.0020 \text{ mol dm}^{-3} \times 0.008 \text{ dm}^3 = c(Pb^{2+}) \times 0.020 \text{ dm}^3$

Therefore, $c(Pb^{2+}) = 0.0020 \text{ mol dm}^{-3} \times 0.008 \text{ dm}^3 / 0.020 \text{ dm}^3 = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$

THEORETICAL PROBLEM 12

Conductometric Titration

Conductivity detector is an electrochemical technique which applies alternating current (AC) signal to two identical electrodes. The applied AC signal induces ions to move in solution and switching of polarity of the AC voltage avoids electrolytic reaction at the electrode. As a result, the mobility of ions in solution relates to the conductivity of ions in solution. Conductivity probe was used in acid-base titration of 25.00 cm^3 HCl *vs* 0.100 mol dm^{-3} NaOH. The conductivity signal was recorded during NaOH addition. The conductometric titration setup is shown in Fig 1. When standard NaOH solution was dropped under gravity force to the titration cell at 3 drops per second and the conductivity value from conductometer recorded, the plot of conductivity of solution *vs* titration time is shown in Fig 2.

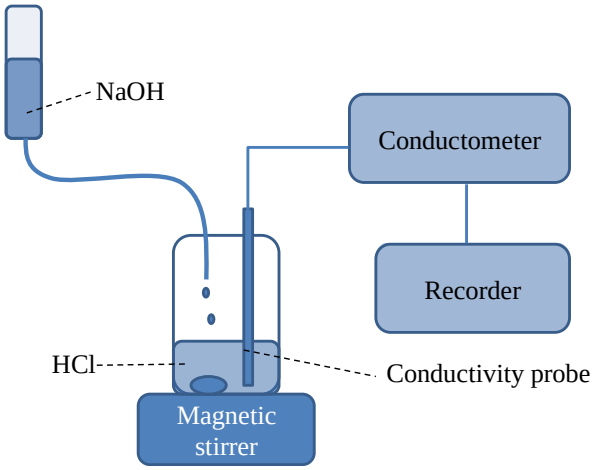


Fig 1. Conductometric titration setup

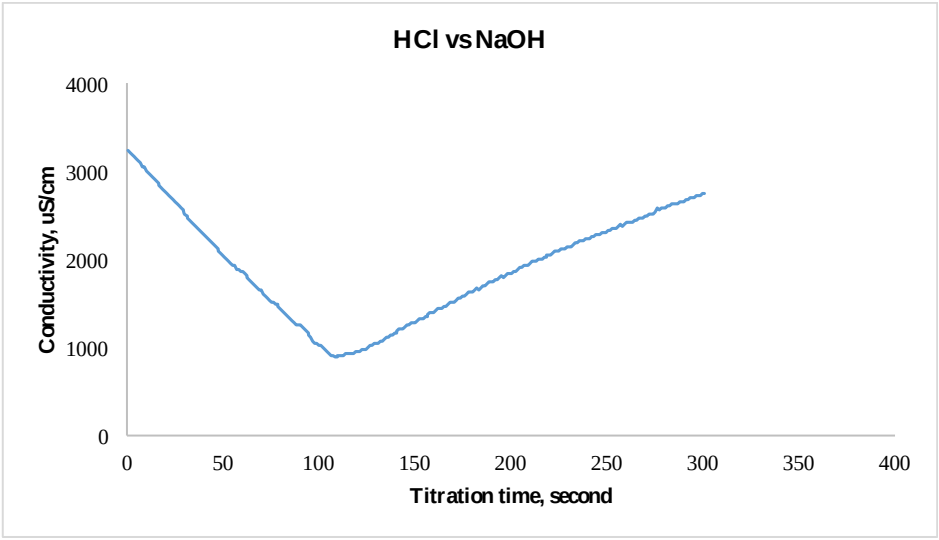


Fig 2. Plot of conductivity of an initial 25.00 cm^3 HCl *vs* titration time.

12.1 Explain why the slope of titration curve before and after the turning point is different.

12.2 Calculate the concentration of HCl, if the volume of NaOH of each drop is 0.029 cm^3 and the turning point is at 108 second.

SOLUTION OF PREPARATORY PROBLEM 12

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

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

Flow rate of NaOH = 3 drops / sec.

Therefore, the volume of NaOH is

108 x 3 = 324 drops = 324 × 0.029 cm^3 = 9.39 cm^3

The concentration of HCl = (9.39 × 0.100) / 25 = 0.038 mol dm^{-3}.

THEORETICAL PROBLEM 13

Titration of Cu and Zn in Metal Alloy

A metal alloy which contains mainly Cu and Zn was analyzed for its metal content. An alloy sample of 2.300 g was placed in a 250 cm^3 Erlenmeyer flask. To this flask, 5.00 cm^3 of mixed acid (concentrated nitric acid and concentrated hydrochloric acid) was added in a fume hood for dissolution of the alloy. The resulting solution was transferred quantitatively into 250 cm^3 volumetric flask and adjusted to volume with deionized water.

A 25.00 cm^3 aliquot of sample solution was adjusted to pH 5.5 and titrated with 0.100 mol dm^{-3} EDTA solution using 1-(2-pyridinezao)-2-naphthol or PAN as indicator. The indicator changed color when 33.40 cm^3 0.100 mol dm^{-3} EDTA was added to the sample solution.

Another 25.00 cm^3 aliquot of sample solution was adjusted to neutral pH and mixed with excess KI. The mixture was then filtered and the resulting solution was titrated against 0.100 mol dm^{-3} sodium thiosulfate using starch solution as indicator. The titration required 29.35 cm^3 sodium thiosulfate to reach the endpoint. Note: $K_{sp(CuI)} = 1.1\times10^{-12}$

13.1 Write the oxidative dissolution reaction(s) of an alloy with nitric acid and hydrochloric acid.

13.2 Determine the %w/w of Cu and Zn in alloy.

SOLUTION OF PREPARATORY PROBLEM 13

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

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

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

n(Cu) by redox titration:

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

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

$n(Cu^{2+})$ = *n*(thiosulfate used) = $29.35 \times 0.1/1000 = 2.935\times10^{-3}$ mol

m(Cu) = 2.935×10^{-3} mol × 63.5 g mol^{-1} = 0.1864 g in 25.00 cm^3 aliquot

Therefore, a 250 cm^3 sample solution will contain 1.864 g

Thus *w*(Cu) = 1.864 g / 2.300 g = 0.81, i.e. 81.0 %

n(Zn) = *n*(total metal) – *n*(Cu) = 3.34×10^{-3} mol – 2.935×10^{-3} mol = 4.05×10^{-4} mol

m(Zn) = 4.05×10^{-4} mol × 65.4 g mol^{-1} = 2.649×10^{-2} g in 25.00 aliquot

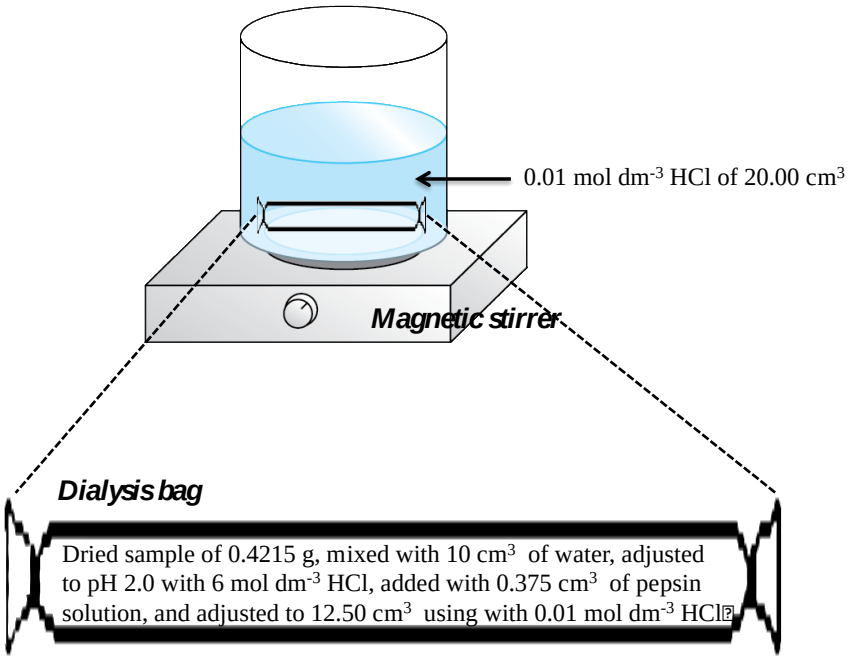
Therefore, 250 cm^3 sample solution will contain 0.2649 g of zinc.

Thus *w*(Zn) = 0.2649 / 2.300 = 0,115, i.e. 11.5 %

THEORETICAL PROBLEM 14

Spectrophotometric determination of iron

To study in vitro gastric digestion of iron, the following procedure is carried out. Dried and homogeneously ground supplement tablet with a mass of 0.4215 g is accurately weighed, mixed with 10 cm^3 of water and adjusted to pH 2.0 with a solution of HCl (6 mol dm^{-3}). Then 0.375 cm^3 of pepsin solution (16% w/v) is added and the mixture is adjusted to 12.50 cm^3 with a HCl solution (0.01 mol dm^{-3}). This mixture was quantitatively transferred into a dialysis bag of a fixed volume, which is further immersed for 2 hours in a 20.00 cm^3 solution of HCl (0.01 mol dm^{-3}). Iron released by gastric digestion is dialyzed until the concentrations of iron inside and outside the dialysis bag are equal.



To determine the gastric digestible iron from the supplement tablet, colorimetric measurement after complex formation between ferrous ion (M) and complexing agent (L) is carried out at pH 5.0. The resulting ML_3 complex exhibits light absorption at 520 nm, whereas M and L do not absorb light at this particular wavelength.

14.1 Under a certain condition that the complexed iron is in the form of ML_3, consider the absorbance values obtained from the total concentration of metal (c_M) and the total concentration of ligand (c_L) in the following table

c_M (mol dm^{-3})	c_L (mol dm^{-3})	Absorbance (at 520 nm) pathlength (b) = 1 cm
6.25×10^{-5}	2.20×10^{-2}	0.750
3.25×10^{-5}	9.25×10^{-5}	0.360

In an excess of L, all of iron is in the form of ML_3.

a) Calculate the molar absorptivity (ε) of ML_3 complex

b) Calculate the overall formation constant (K_f) of ML_3 complex

14.2 The CHN analysis shows that the complexing agent (L) contains 80 % of C, 4.44 % of H, and 15.56 % of N. The molar mass of this compound is 180 g mol^{-1} Determine the molecular formula of L.

14.3 The Fe^{2+} complexes (ML, ML_2 and ML_3) adopt the octahedral structure. (Assume a perfect octahedral geometry for each isomer of these three complexes). Sketch the d-orbital splitting diagram for ML_3. Draw all possible isomers of Fe^{2+} complexes. Order the magnitudes of Δ_o (crystal field splitting) of these three complexes and explain.

Spectrochemical series:

$I^- < Br^- < Cl^- \approx SCN^- < F^- \approx$ urea $< ONO^- \approx OH^- < H_2O < NCS^- <$ pyridine $\approx NH_3 <$ en $<$ bipy $<$ *o*-phen $< NO_2^- < CN^- \approx CO$)

14.4 To determine the dialyzable iron concentration (iron outside the dialysis bag), 5.00 cm^3 of the solution outside the dialysis bag is added with a reducing agent to ensure that all of dissolved iron is in the ferrous ion form. Then, the solution is adjusted to the suitable pH, followed by addition of excess amount of complexing agent (L) and deionized water added to make up the volume to 50.00 cm^3 in a volumetric flask. The absorbance measured at 520 nm is 0.550. Calculate the concentration of dialyzable iron (in unit of mg dm^{-3}).

14.5 Presume all of the iron in the supplement tablet is completely digestible in the gastric condition. Determine in mg the iron in 1.0000 g of supplement tablet.

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SOLUTION OF PREPARATORY PROBLEM 14

14.1 a) At $c_L = 2.20\times10^{-2}$ mol dm^{-3}, $[ML_3] = 6.25\times10^{-5}$

$A = \varepsilon bc$, therefore $\varepsilon = A / bC = 0.750 / 6.25\times10^{-5} = 12{,}000$ L mol^{-1} cm^{-1}

b) $M + 3\,L \rightleftharpoons ML_3$

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

at $c_L = 9.25\times10^{-5}$ mol dm^{-3}, $[ML_3] = 0.360 / 12000$

$[ML_3] = 3.0\times10^{-5}$ (2)

therefore, $[M] = (3.25\times10^{-5}) - (3.0\times10^{-5})$

$[M] = 0.25\times10^{-5}$ (3)

$[L] = (9.25\times10^{-5}) - 3 \times (3.0\times10^{-5})$

$[L] = 0.25\times10^{-5}$ (4)

Hence $K_f = (3.0\times10^{-5}) / (0.25\times10^{-5})\,(0.25\times10^{-5})^3$

$K_f = 7.68\times10^{17}$

14.2 n(C) : n(H) : n(N) = 80/12 : 4.44/1 : 15.56/14 = 6.67 : 4.44 : 1.11 = 6 : 4 : 1

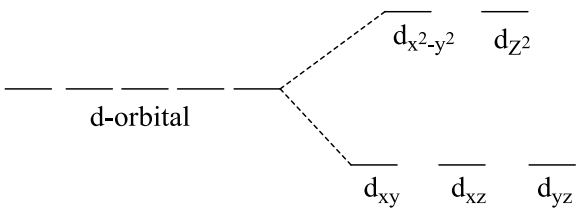
Therefore, the empirical formula of L is C_6H_4N

The empirical molar mass = (6×12) + (4×1) + (1×14) = 90 g mol^{-1}

Molar mass/ empirical molar mass = 180 g mol^{-1} / 90 g mol^{-1} = 2

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

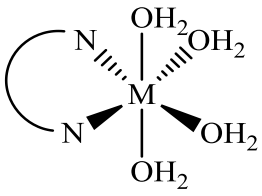
14.3 d-orbital splitting diagram for ML_3



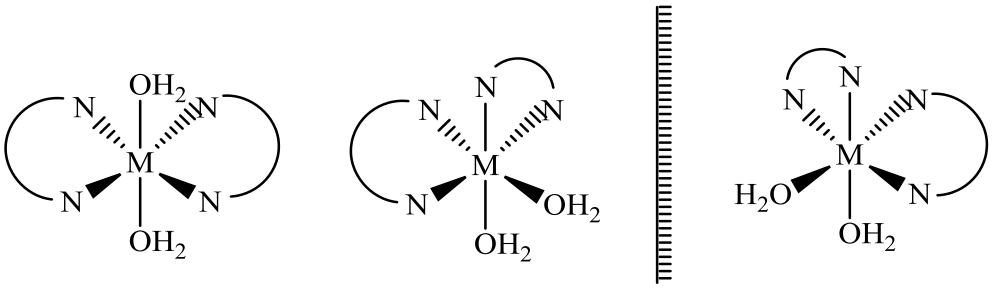
Octahedral field

Possible isomers of Fe^{2+} complexes

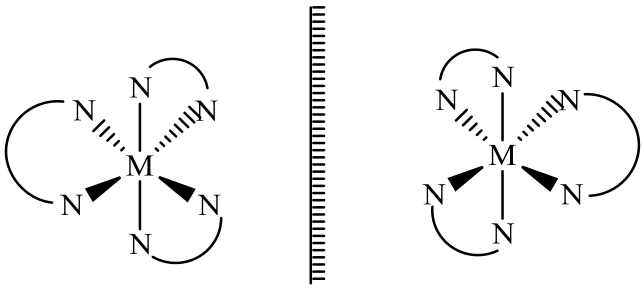
ML :



ML_2 :



ML_3 :



Δ_o of ML < ML_2 < ML_3 ∵ H_2O is a weaker field ligand when compared with bipyridine.

14.4 A = ε b c, therefore c = A / ε b = 0.550 / 12000 = 4.58×10^{-5} mol dm^{-3}

The concentration of dialyzable iron is:

4.58×10^{-5} mol dm^{-3} × 50.00 / 5.00 = 4.58×10^{-4} mol dm^{-3}

4.58×10^{-4} mol dm^{-3} × 55.845 g mol^{-1} = 0.02558 g dm^{-3} = 25.58 mg dm^{-3}

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

The total volume is 12.50 cm^3 (inside the dialysis bag) + 20.00 cm^3 (outside the bag) = 32.50 cm^3.

Therefore, the total amount of digestible iron is:

(25.58 mg dm^{-3} × 32.50 cm^3) = 0.8314 mg

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

For the supplement of 1.0000 g, the iron content is

0.8314 mg × 1.0000 g / 0.4215 g = 1.972 mg

THEORETICAL PROBLEM 15

Basic Electrochemistry

Consider the following electrochemical cell:

$Pt(s) \mid MnO_4^-$ (0.00100 mol dm^{-3}), Mn^{2+}(0.00200 mol dm^{-3}), pH=3.00 $\parallel$ $\parallel$ Ce^{4+}(0.0100 mol dm^{-3}), Ce^{3+}(0.0100 mol dm^{-3}) $\mid$ Pt(s)

The relevant reduction half-reactions are:

$Ce^{4+} + e^- \longrightarrow Ce^{3+}$ $\qquad E^o = 1.70$ V

$MnO_4^- + 8\ H^+ + 5e^- \longrightarrow Mn^{2+} + 4\ H_2O$ $\qquad E^o = 1.507$ V

15.1 Write a balanced net reaction for this cell and determine the values of E^o_{cell} and K for the net reaction.

15.2 How many Coulombs of electron charge are transferred when 5.0 mg of Ce^{4+} are consumed in the reaction from question 15.1?

15.3 Determine the cell potential for the electrochemical cell shown in the cell diagram.

SOLUTION OF PREPARATORY PROBLEM 15

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

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

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

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

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

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

$$E^o_{cell} = \frac{0.05916}{5} \log K$$

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

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

15.2

$$5\ \text{mg}\ Ce^{4+}\left(\frac{1\ \text{g}}{1000\ \text{mg}}\right)\left(\frac{1\ \text{mol}\ Ce^{4+}}{140.12\ \text{g}\ Ce^{4+}}\right)\left(\frac{5\ \text{mol}\ e^-}{5\ \text{mol}\ Ce^{4+}}\right)\left(\frac{96.485\ \text{C}}{1\ \text{mol}\ e^-}\right) = 3.44\ \text{C}$$

15.3

$$E_{cell} = E^o_{cell} - \frac{0.05916}{n}\log Q$$

Where Q is a reaction quotient.

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

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

$E_{\text{cell}} = 0.481\text{V}$

THEORETICAL PROBLEM 16

Calculation of concentration

16.1 What is the concentration of Cu^{2+} (in mol dm^{-3}) in a solution prepared by mixing of 1.345 g $CuCl_2$ with 50.00 cm^3 of $CuSO_4$ solution with a mass concentration 31.9 g dm^{-3} and adjusting the volume to 500 cm^3 by a HCl solution (c = 0.01 mol dm^{-3})?

16.2 Calculate whether a precipitate will be formed if 25.00 cm^3 aliquot of the resulting solution in 16.1 is adjusted to pH 8.0 with NaOH and the final volume is 100.0 cm^3. Note: $K_{sp(Cu(OH)_2)} = 4.8\times10^{-20}$

SOLUTION OF PREPARATORY PROBLEM 16

16.1 - $M(CuCl_2)$ = 134.45 g mol^{-1}

$n(Cu^{2+})$ in 1.345 g of $CuCl_2$ = 1.345 g / 134.45 g mol^{-1} = 0.0100 mol

- $M(CuSO_4)$ = 159.62 g mol^{-1}

$n(Cu^{2+})$ in 50.00 cm^3 of $CuSO_4$ solution:

$n(Cu^{2+}) = n(CuSO_4) = m(CuSO_4) / M(CuSO_4) =$

$= [c_m(CuSO_4) \times V(CuSO_4)] / M(CuSO_4) =$

$= (31.9\ g\ dm^{-3} \times 0.050\ dm^3) / 159.62\ g\ mol^{-1} = 0.0100$ mol

Therefore, the total amount of substance of Cu^{2+} is 0.0100 + 0.0100 = 0.0200 mol

Since 500 cm^3 of the resulting solution contains 0.0200 mol Cu^{2+},

the concentration of Cu^{2+} in the solution is 0.0400 mol dm^{-3}.

16.2 - The concentration of Cu^{2+} in the resulting solution is: 0,04 mol dm^{-3} / 4 = 0.01 mol dm^{-3}

- pH = 8.0, implying that $[OH^-] = 1\times10^{-6}$

$[Cu^{2+}][OH^-]^2 = (1\times10^{-2}) \times (1\times10^{-6})^2 = 1\times10^{-14}$ is greater than $K_{sp}(Cu(OH)_2)$,

i.e. 4.8×10^{-20}, and, therefore, the precipitate of $Cu(OH)_2$ is formed.

THEORETICAL PROBLEM 17

Small molecule activation by frustrated Lewis pairs

Electron acceptors and electron donors are usually called Lewis acids and Lewis bases, respectively.

17.1 Trispentafluorophenylborane is a well-known Lewis acid for the polymerization of olefin. Propose a reaction to prepare trispentafluorophenyborane from boron trichloride and bromopentafluorobenzene.

17.2 The steric hindrance precludes the formation of classical bonds between Lewis acid and Lewis base. Propose a structure of Frustrated Lewis Pairs from the reaction of $B(C_6F_5)_3$ and $PH(t\text{-}Bu)_2$ if a zwitterion product is only obtained. (See Reference: Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124-1126.)

17.3 Propose a reaction between the obtained zwitterion in 17.2 and Me_2SiHCl.

17.4 Show the structure of the product obtained from the $B(C_6F_5)_3$ and $P(t\text{-}Bu)_3$ under hydrogen gas atmosphere.

17.5 If HD is used instead of dihydrogen gas, write down all possible products.

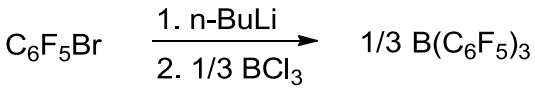
17.6 Only one product is obtained from the reaction of $B(C_6F_5)_3$ and $P(t\text{-}Bu)_3$ under ethylene gas atmosphere. Draw its structure.

17.7 Draw the structure of the product if the reaction of the isolated product from 17.6 is carried out under nitric oxide gas atmosphere.

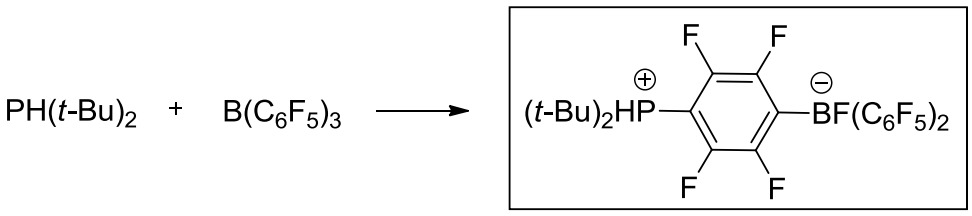
17.8 Only one product is obtained from the reaction of $B(C_6F_5)_3$ and $P(t\text{-}Bu)_3$ under carbon dioxide gas atmosphere. Draw its structure.

SOLUTION OF PREPARATORY PROBLEM 17

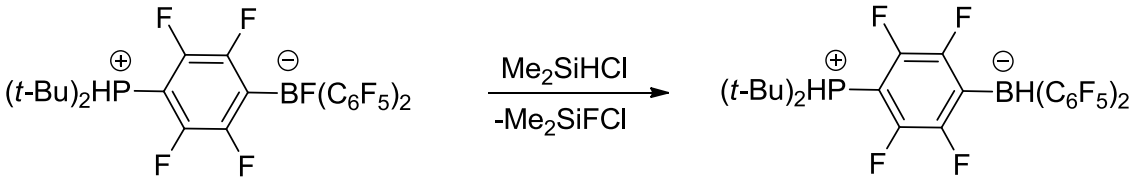
17.1



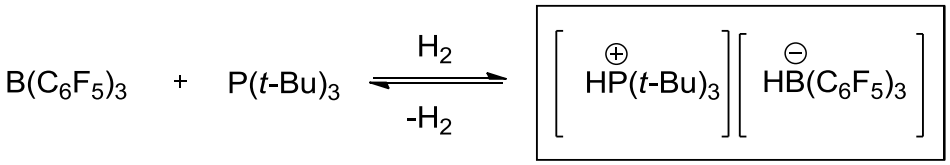
17.2



17.3



17.4



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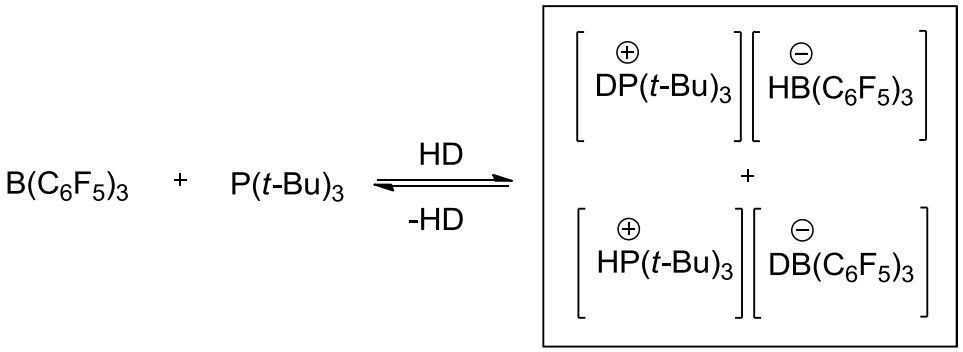
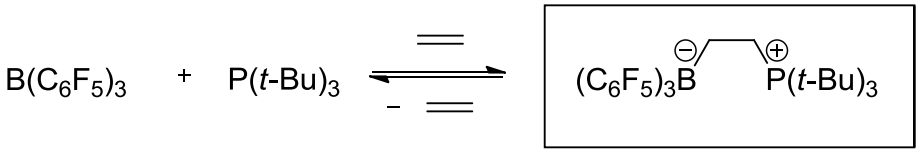
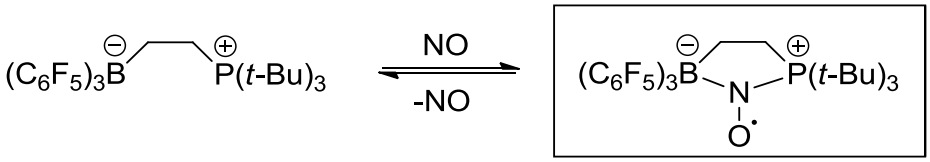


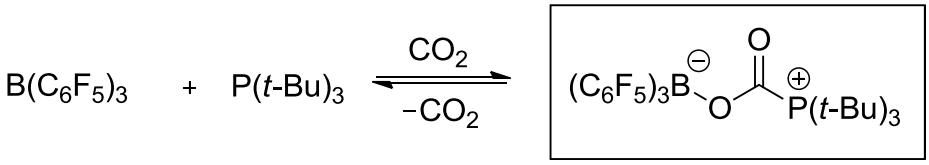
17.6



17.7


(C6F5)3B
P(t-Bu)3
NO
-NO
(C6F5)3B
N
O
P(t-Bu)3

17.8


B(C6F5)3
+
P(t-Bu)3
CO2
−CO2
(C6F5)3B
O
O
P(t-Bu)3

THEORETICAL PROBLEM 18

Silver iodide

The crystalline structure of β-AgI is similar to that of ice, allowing it to induce freezing by the process known as heterogeneous nucleation (cloud seeding). β-AgI is a bright yellow solid and has the wurtzite structure.

18.1 When the solid silver iodide is exposed to sunlight, it will darken rapidly. What is the oxidation state of silver in the darkened solid?

18.2 What is the solubility trend in AgF, AgCl, AgBr, AgI?

18.3 Consider:

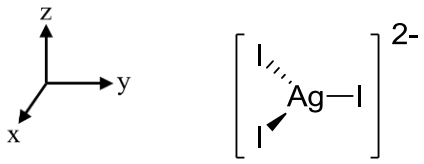
(a) $Ag^+(aq) + e^- \longrightarrow Ag(s)$ $\quad E^o = +0.80$ V

(b) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ $\quad K_{sp} = 8.51\times10^{-17}$

(c) $Ag^+(aq) + 3\,I^-(aq) \rightleftharpoons [AgI_3]^{2-}(aq)$ $\quad K = 10^{14}$

From the given information, find the standard reduction potential of $[AgI_3]^{2-}$.

18.4 The salt $[PPh_3Me]_2[AgI_3]$ contains a triiodoargentate(I) ion $[AgI_3]^{2-}$ with approximate trigonal planar geometry. (See reference: Bowmaker, G. A.; Camus, A.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans*., **1990**, 727-731.) The structure of $[AgI_3]^{2-}$ is shown below. Draw the crystal field splitting diagram for the *d* orbitals of silver and fill in all appropriate electrons.



SOLUTION OF PREPARATORY PROBLEM 18

18.1 Oxidation state of silver: 0

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

18.2 AgF > AgCl > AgBr > AgI

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

18.3 – 0.028 V

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

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

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

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

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

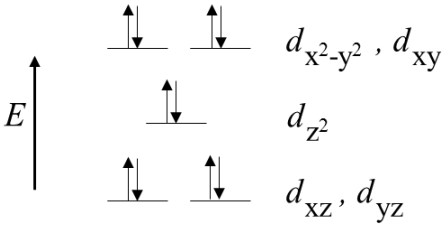
(d) $[AgI_3]^{2-}(aq) + e^- \rightleftharpoons Ag(s) + 3\,I^-(aq)$

Eqn (d) = (a) – (c)

Therefore, $\Delta G^o_d = \Delta G^o_a - \Delta G^o_c = -77{,}200 - (-79{,}867) = 2{,}667$ J mol^{-1}

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

18.4 For trigonal planar,



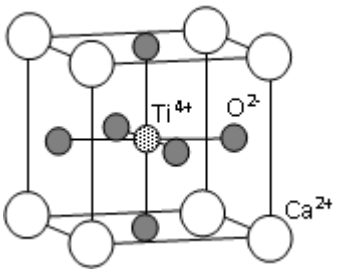
The ligands lie in the xy plane, then the $d_{x^2-y^2}$ and d_{xy} orbitals that have their electron density concentrated in this plane will have the highest energy. The d_{xz} and d_{yz} orbitals have their electron density out of this xy plane, so their energies are the lowest. The d_{z^2} orbital has its electron density mostly out of the xy plane, but there is a ring of electron density in the xy plane, so the d_{z^2} orbital will have energy higher than the d_{xz} and

d_{yz} orbitals but still lower than the $d_{x^2-y^2}$ and d_{xy} orbitals. In addition, the number of *d*-electrons for silver in $[AgI_3]^{2-}$ is 10. Therefore, all *d*-orbitals should be filled.

THEORETICAL PROBLEM 19

Perovskite structure

A mineral perovskite crystallizes in the cubic unit cell in which Ca^{2+} and O^{2-} ions constitute a ccp arrangement and Ti^{4+} ion occupies an interstitial hole as shown here.



19.1 Based on the unit cell above, what is the empirical formula of perovskite?

19.2 Name types of interstitial holes present in the ccp unit cell. How many holes are there, for each type, within the unit cell?

19.3 From your answer in 19.2, which type of interstitial hole is occupied by Ti^{4+} ion?

SOLUTION OF PREPARATORY PROBLEM 19

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

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

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

Therefore, the empirical formula is $CaTiO_3$.

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

19.3 Octahedral hole

THEORETICAL PROBLEM 20

Quantum Numbers and Atomic Orbitals

20.1 Each of the following sets of quantum numbers is not permissible for an orbital. Why?

	n	l	m_l	m_s
(i)	1	1	0	+1/2
(ii)	3	1	-2	-1/2
(iii)	2	-1	0	+1/2

20.2 Give the notation for the subshells denoted by the following quantum numbers:

(i) $n = 6,\ \ l = 2$

(ii) $n = 4,\ \ l = 3$

(iii) $n = 6,\ \ l = 1$

20.3 What is the number of different orbitals in each of the following subshells?

(i) 3*d*

(ii) $n = 5, l = 3$

(iii) $n = 3, l = 0$

SOLUTION OF PREPARATORY PROBLEM 20

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

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

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

20.2 (i) 6*d*

(ii) 4*f*

(iii) 6*p*

20.3 (i) five

(ii) seven

(iii) one

THEORETICAL PROBLEM 21

Radioactivity of Iodine and Nuclear Equations

21.1 The half-life of ^{131}I is 8 days. If a freshly prepared solution of ^{131}I has a concentration of 0.1 mol dm^{-3},

(i) what will be the concentration of ^{131}I after 2 half-lives?

(ii) what will be the concentration of ^{131}I after 40 days?

21.2 Identify X in each of the following nuclear equations:

(i) $X \rightarrow {}^{14}_{7}N + \beta^-$

(ii) ${}^{38}_{19}K \rightarrow {}^{38}_{18}Ar + X$

(iii) ${}^{55}_{26}Fe + {}^{0}_{-1}e \rightarrow X$

(iv) $X \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$

(v) ${}^{14}_{7}N + X \rightarrow {}^{14}_{6}C + {}^{1}_{1}H$

(vi) ${}^{110m}_{47}Ag \rightarrow X + \gamma$

(vii) ${}^{1}_{0}n + {}^{235}_{92}U \rightarrow {}^{136}_{53}I + X + 4\,{}^{1}_{0}n$

(viii) ${}^{2}_{1}H + {}^{3}_{1}H \rightarrow X + {}^{1}_{0}n$

SOLUTION OF PREPARATORY PROBLEM 21

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

[I-131] 0.1 mol dm^{-3} ⟶ 0.05 mol dm^{-3} ⟶ **0.025 mol dm^{-3}**

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

[I-131]

0.1 mol dm^{-3} ⟶ 0.05 mol dm^{-3} ⟶ 0.025 mol dm^{-3} ⟶ 0.0125 mol dm^{-3} ⟶ 6.25 × 10^{-3} mol dm^{-3} ⟶ **3.125 × 10^{-3} mol dm^{-3}**

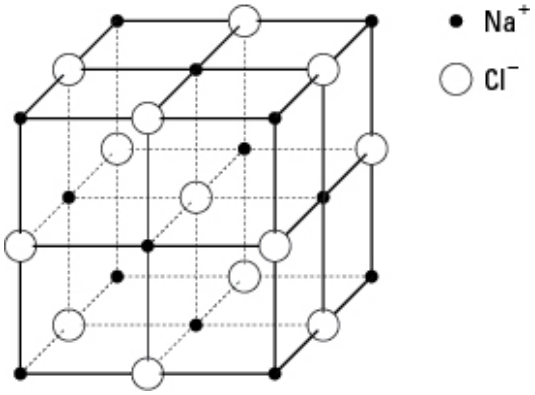
21.2 (i) $^{14}_{6}\mathrm{C}$ (ii) $^{0}_{+1}e$ or β^{+} (iii) $^{55}_{25}\mathrm{Mn}$ (iv) $^{238}_{92}\mathrm{U}$

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

THEORETICAL PROBLEM 22

Structure and Chemistry of Sodium Chloride

22.1 The unit cell of NaCl is shown below:



(i) What is the coordination number of Na^+ and Cl^-?

(ii) What is the number of formula units in the unit cell?

(iii) If the length of the unit cell of NaCl is 560 pm and the mass of NaCl is 58.5 g mol^{-1}, what is the density of NaCl?

22.2 NaCl can be prepared by a reaction between Na(*s*) and Cl_2(*g*):

$$Na(s) + \tfrac{1}{2} Cl_2(g) \rightarrow NaCl \qquad \Delta H_{formation} = -411 \text{ kJ}$$

(i) What are the values of *n* and *l* for the valence electrons of a Na atom?

(ii) Compare the size of Na vs. Cl and Na^+ vs. Cl^-.

(iii) Draw the Lewis structure of Cl_2.

(iv) Calculate the lattice energy of NaCl.

$\Delta H_{sublimation}$ for Na = 107 kJ mol^{-1}, IE_1 for Na = 496 kJ mol^{-1},

Cl–Cl dissociation = 244 kJ mol^{-1}, electron affinity of Cl = –349 kJ mol^{-1}

22.3 Chemistry of NaCl:

(i) Write the reaction between NaCl(*aq*) and Br_2(*l*).

(ii) Write the ionic equation between NaCl(*aq*) and $AgNO_3$(*aq*).

(iii) What is the flame color when NaCl is placed in the flame?

SOLUTION OF PREPARATORY PROBLEM 22

22.1 (i) 6 and 6

(ii) 4

(iii) 2.21 g cm^{-3}

Density = m/V

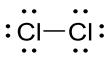
$V = a^3 = (560\ pm)^3 = 1.76\times10^{-22}\ cm^3$

$m = (4 \times 58.5\ g) / (6.022\times10^{23}) = 3.89\times10^{-22}\ g$

Density = $3.89\times10^{-22}\ g / 1.76\times10^{-22}\ cm^3 = 2.21\ g\ cm^{-3}$

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

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

(iii) 

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

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

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

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

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

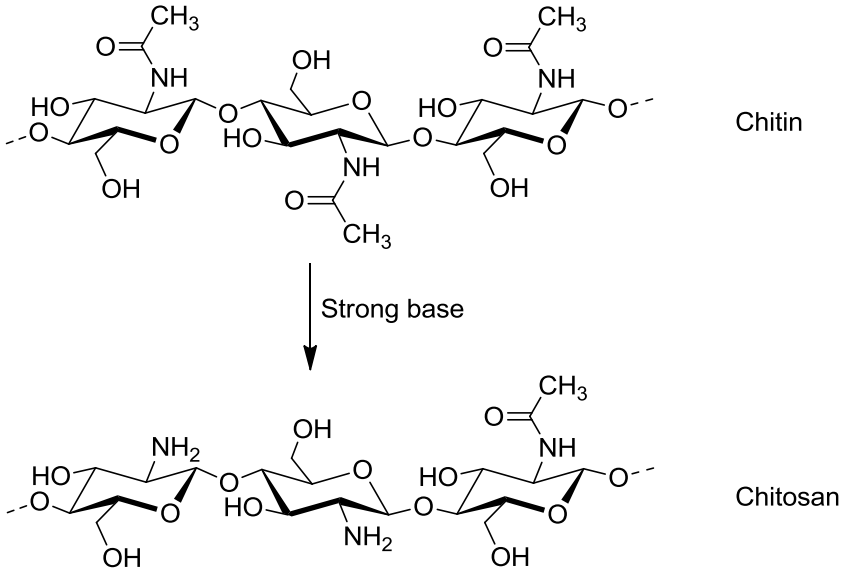
(ii) $Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$

(iii) Yellow

THEORETICAL PROBLEM 23

Natural Chelator from Shrimp Shell

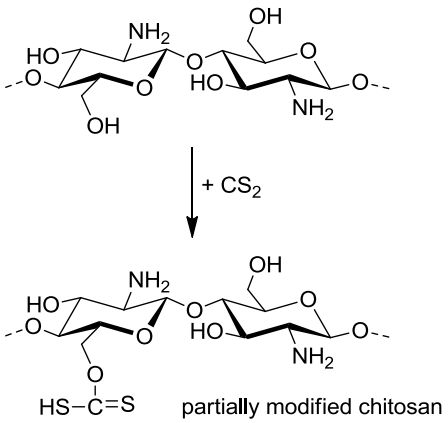
Chitosan is a linear polysaccharide composed of *β*-(1-4)-linked *D*-glucosamine (deacetylated unit) and *N*-acetyl-*D*-glucosamine (acetylated unit). It is made by treating the chitin shells of shrimp or other crustaceans with a strong base, like sodium hydroxide. The deacetylation of chitin by a strong base yields partially-acetylated chitosan as shown below:



Chitosan can be used for a variety of purposes like helping plants to fight off fungal infections, preventing spoilage in wine, helping deliver drugs through the skin, being applied to reduce bleeding, and as an antibacterial agent. In the environmental aspect, chitosan can be used as an effective metal ion adsorbent. The adsorption capacities of chitosan for Cu(II), Hg(II), Pb(II) and Zn(II) are 79.94, 109.55, 37.2, 47.15 mg (g chitosan)$^{-1}$, respectively.

23.1 Suggest the preferred binding sites in completely-deacetylated chitosan for metal ion.

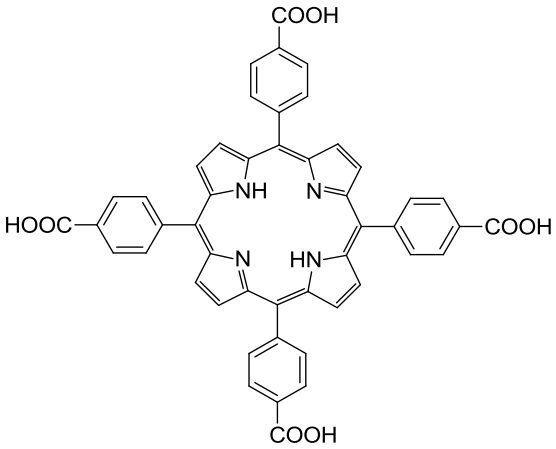
The selectivity of chitosan towards Pb^{2+} can be increased by modification with CS_2 yielding partially modified chitosan (PMCS) as in the structure below:



The absorption capacity toward Pb^{2+} was increased from 37.2 to 156.0 mg g^{-1} chitosan (Wang, N.; Zheng, P.; Ma, X. *Powder Technol*. **2016**, *301*, 1-9.)

23.2 Suggest the most preferred site(s) in chitosan for Pb^{2+} and draw the bond(s) between that preferred site(s) and Pb^{2+}. Explain the increase in absorption capacity of PMCS toward Pb^{2+}.

To increase the sensitivity of the chitosan toward metal ion, the dye like *meso*-tetra(*p*-carboxyphenyl)porphyrin is chemically bonded with chitosan matrix. After the two acidic protons are removed, the four nitrogen atoms will bind with metal ion. The two axial sites of the metal ion normally bind with water molecules yielding the octahedral complex. Each metal ion gives characteristic absorption maximum in the visible range.

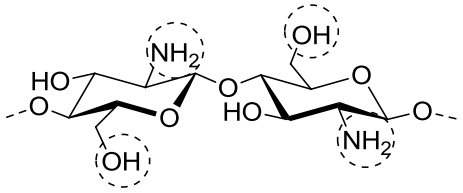


23.3 Suggest the bonds between *meso*-tetra(*p*-carboxyphenyl)porphyrin and chitosan if a weak protonic acid is used as a catalyst.

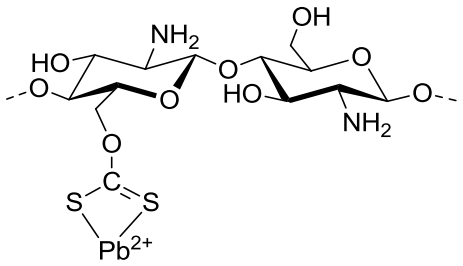
23.4 If Fe^{2+} is being adsorbed by the chitosan-porphyrin adsorbent, draw the structure of the complex and predict the approximate *d*-orbital splitting in the proposed complex.

SOLUTION OF PREPARATORY PROBLEM 23

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

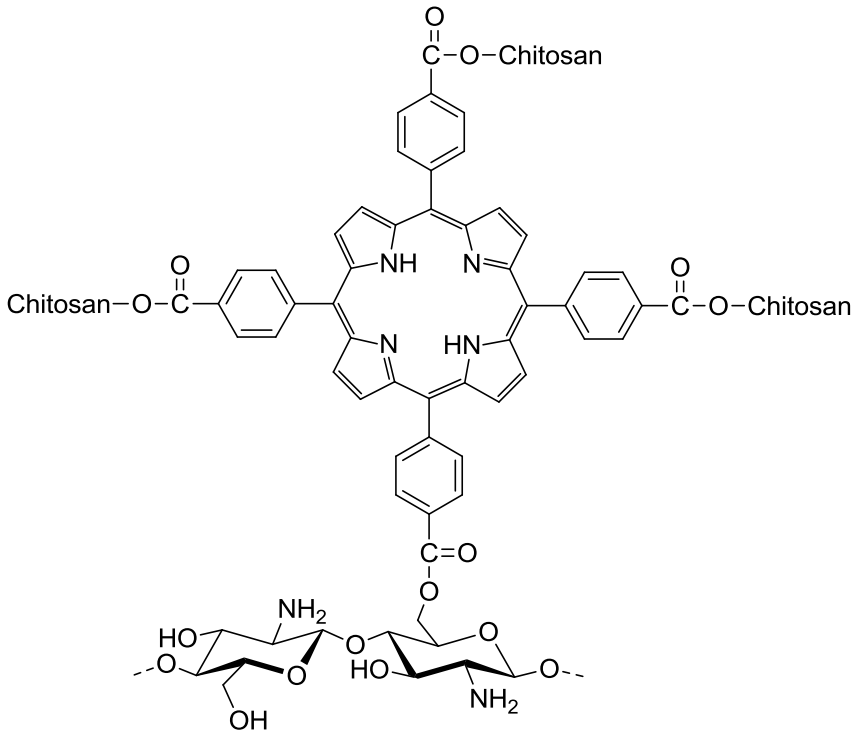


23.2

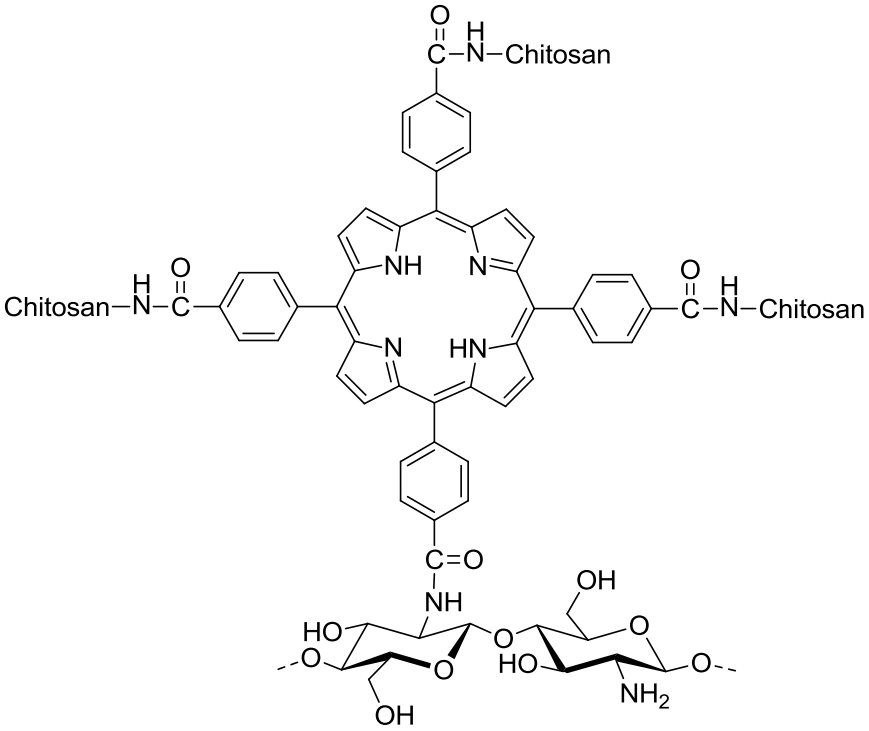


Pb^{2+} is a soft metal ion so it prefers to form bond with sulfur. This helps PMCS adsorb Pb^{2+} better.

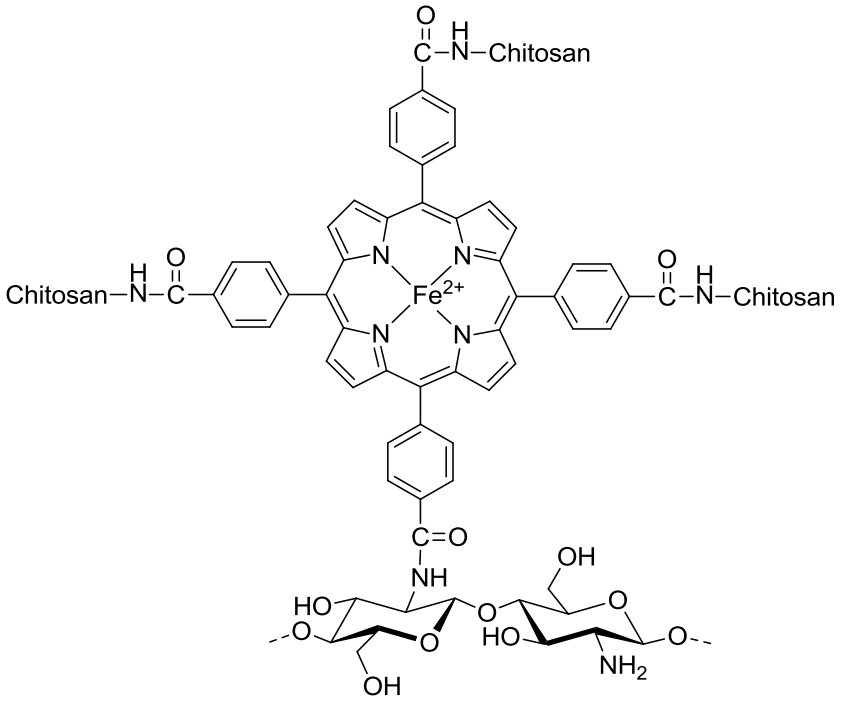
23.3 *meso*-tetra(*p*-carboxyphenyl)porphyrin can form ester bond with chitosan as shown in the proposed structure below:



Or amide bonds are formed as below:

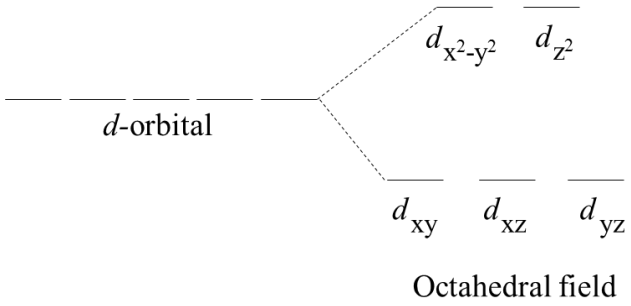


23.4 One of the structures in question 23.3 was chosen to bond with Fe^{2+} as the proposed structure below.



The two vacant axial sites are bonding with water molecules.

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



THEORETICAL PROBLEM 24

Compound Identification and Related Chemistry

A reaction between **M** and Cl_2 gives the only product $\mathbf{M}_x Cl_y$. The following results are obtained under various conditions:

M (mol)	Cl_2 (mol)	Product (g)
0.20	0.80	26.7
0.30	0.70	40.0
0.40	0.60	53.3
0.50	0.50	44.4
0.60	0.40	35.6
0.70	0.30	26.7
0.80	0.20	17.8

24.1 What is the chemical formula of $\mathbf{M}_x Cl_y$? Identify **M**.

24.2 Write balanced chemical equations of:

(i) complete hydrolysis of $\mathbf{M}_x Cl_y$

(ii) $\mathbf{M}_x Cl_y + H_2SO_4$

24.3 At certain temperatures, $\mathbf{M}_x Cl_y$ exists in equilibrium as a dimer:

$$\mathbf{M}_x Cl_y \rightleftharpoons (\mathbf{M}_x Cl_y)_2$$

Draw a chemical structure of the dimer.

SOLUTION OF PREPARATORY PROBLEM 24

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

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

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

Thus, the chemical formula of $\mathbf{M}_x Cl_y$ = **M**Cl_3

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

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

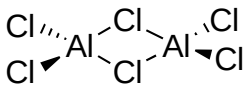
Atomic mass of **M** = 133 – (3 × atomic mass Cl) = 133.3 – (3 × 35.45) = 26.9 g mol^{-1}

Thus: **M** = Al

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

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

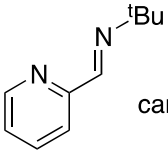
24.3



THEORETICAL PROBLEM 25

Isomerism of Octahedral Fe Complexes

$Fe(N,N')_2Cl_2$ has an octahedral structure featuring two bidentate, neutral α-imino-pyridine (N,N') ligands, whose structure is shown below.



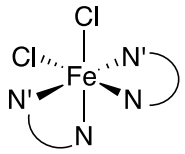
can be drawn as:

25.1 Draw all possible isomers of $Fe(N,N')_2Cl_2$.

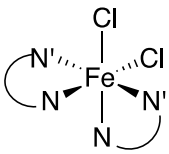
25.2 Which isomers of $Fe(N,N')_2Cl_2$ are optically active?

SOLUTION OF PREPARATORY PROBLEM 25

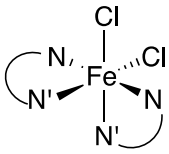
25.1



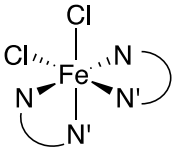
isomer **A**
cis(Cl,Cl)
trans(N',N'), *cis*(N,N)



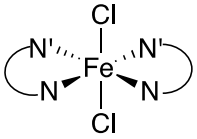
isomer **A***
cis(Cl,Cl)
trans(N',N'), *cis*(N,N)



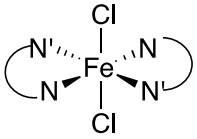
isomer **B**
cis(Cl,Cl)
cis(N',N'), *trans*(N,N)



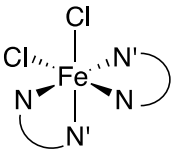
isomer **B***
cis(Cl,Cl)
cis(N',N'), *trans*(N,N)



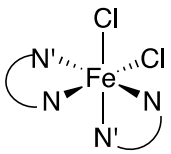
isomer **C**
*trans(*Cl,Cl)
cis(N',N'), *cis*(N,N)



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



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



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

25.2 Isomers **A**, **A***, **B**, **B***, **E**, and **E***

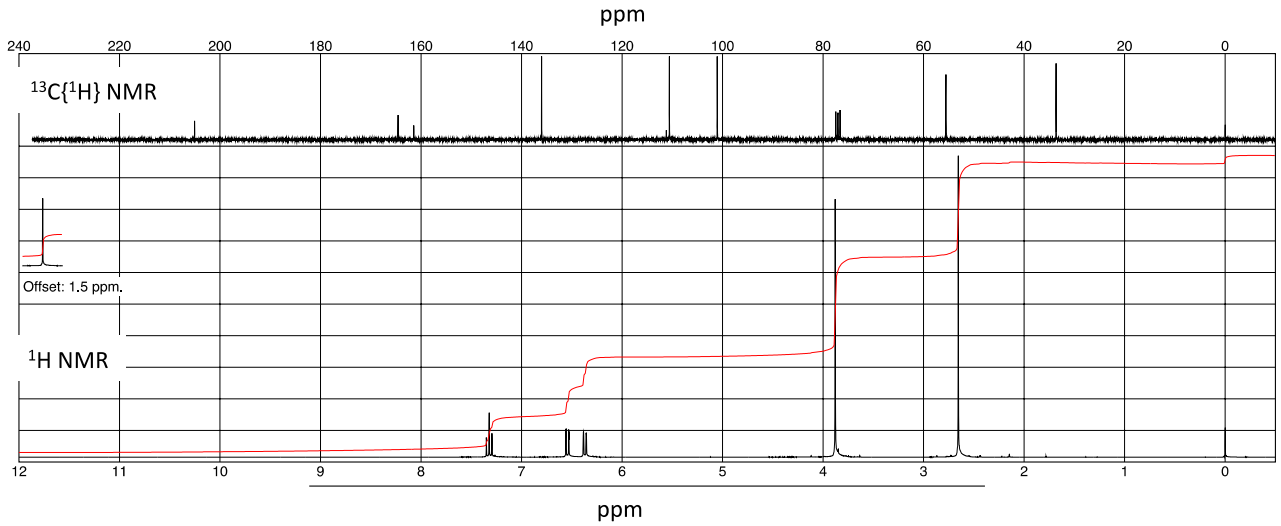
THEORETICAL PROBLEM 26

Stoichiometry and Structure Determination

Compound **A** consists only of three elements C, H, and O. Under standard conditions, **A** is a yellow solid with a molar mass of 166.2 g mo1^{-1}. By weight, **A** has 28.9% O and 65.0% C.

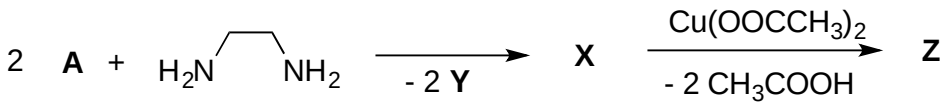
26.1 Determine chemical formula of **A**.

26.2 **A** contains a phenol functional group with intramolecular hydrogen bonding. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **A** in $CDCl_3$ are shown below. Based on your answer in 26.1, draw a chemical structure of **A**, and show the intramolecular hydrogen bond(s).



**NMR data were obtained from Sigma-aldrich.com.*

26.3 From the reaction scheme below, draw chemical structures of **X**, **Y**, and **Z**.



SOLUTION OF PREPARATORY PROBLEM 26

26.1

% by mass C : H : O = 65.0 : 6.10 : 28.9

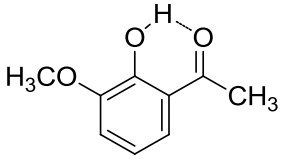
$$\text{\% by mol C : H : O} = \frac{65.0}{12.0} : \frac{6.10}{1.01} : \frac{28.9}{16.0}$$

$$= 5.42 : 6.04 : 1.81$$

$$\text{C : H : O} = 9 : 10 : 3$$

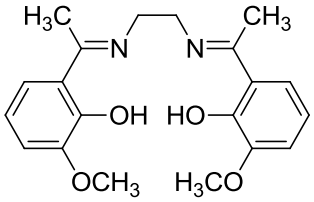
The formula of the compound is: $C_9H_{10}O_3$

26.2



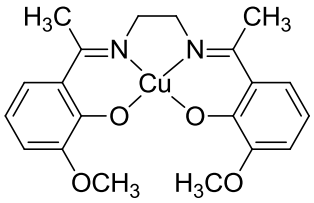
26.3

X =



Y = 

Z =



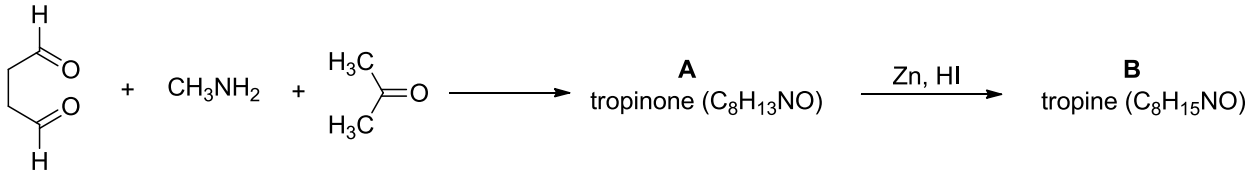
THEORETICAL PROBLEM 27

Atropine

Atropine is an organic compound used to treat certain types of nerve agent and pesticide poisonings. This compound can be synthesized from tropine and tropic acid in one step.

Tropine can be prepared as shown in the scheme below. The first step of this synthesis is “double Mannich reaction” (Robinson, 1917).

27.1 Write down the structural formulae of compounds **A** and **B**.



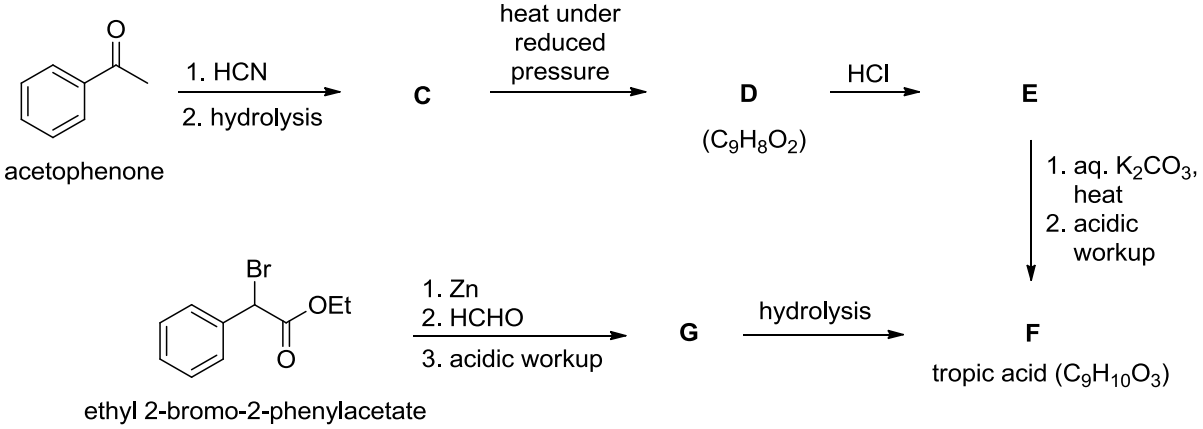
Tropic acid can be prepared from the reaction of acetophenone and HCN followed by hydrolysis, elimination, addition and nucleophilic substitution (Mackenzie and Ward, 1919). In this synthesis, it should be noted that the electrophilic addition by HCl did not follow Markovnikov's Rule, and the anti-Markovnikov product (**E**) was obtained.

Tropic acid (**F**) can also be prepared in only three steps from ethyl 2-bromo-2-phenylacetate and paraformaldehyde (Pernot, 1950). NMR data of tropic acid (**F**) are provided below.

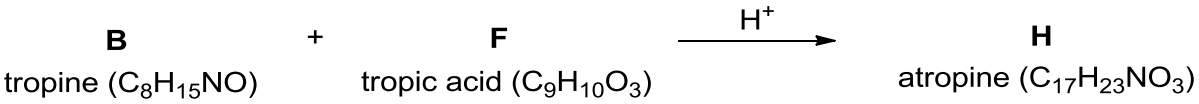
^{1}H NMR (400 MHz, d-DMSO): δ 12.35 (br, s, 1H), 7.34-7.25 (m, 5H), 4.91 (br s, 1H), 3.91 (dd, *J* = 10.0, 8.4 Hz, 1H), 3.64 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.56 (dd, *J* = 10.0, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, d-DMSO) δ 173.7, 137.1, 128.4, 128.0, 127.1, 63.4, 54.3

xxxf27.2 Write down the structural formulae of compounds **C**-**G** in the diagram below.

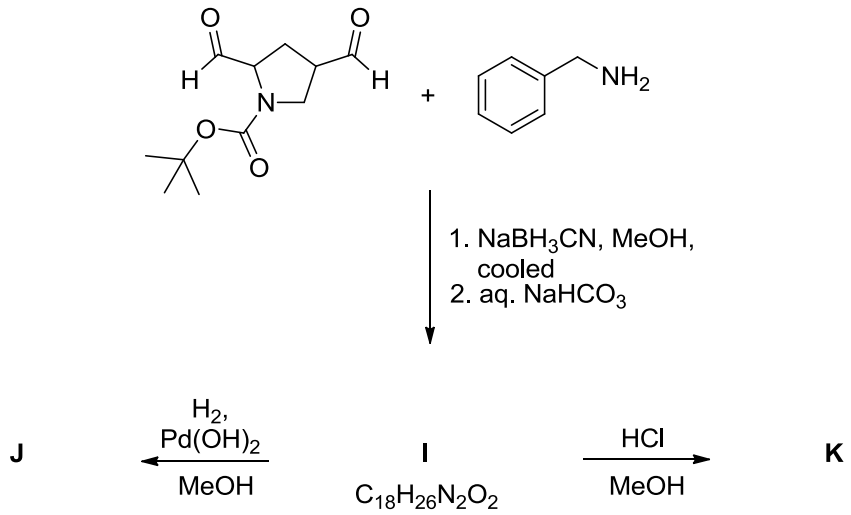


When tropine was combined with tropic acid under acidic conditions, atropine was produced.



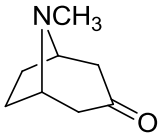
27.3 Write down the structural formula of atropine.

27.4 Predict the major products of the reactions shown below. ^{13}C NMR spectrum of compound **I** shows nine signals in the range of 0 – 80 ppm, four signals in the range of 120 – 140 ppm, and one signal at 155 ppm. ^{13}C NMR spectrum of compound **J** shows eight signals in the range of 0-80 ppm and one signal at 155 ppm. ^{13}C NMR spectrum of compound **K** shows seven signals in the range of 0 – 80 ppm and four signals in the range of 120 – 140 ppm.

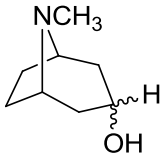


SOLUTION OF PREPARATORY PROBLEM 27

27.1

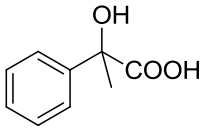


A
tropinone ($C_8H_{13}NO$)

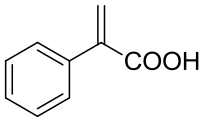


B
tropine ($C_8H_{15}NO$)

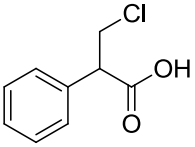
27.2



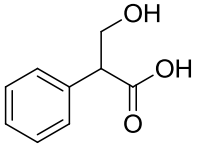
C



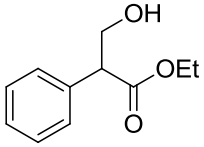
D



E

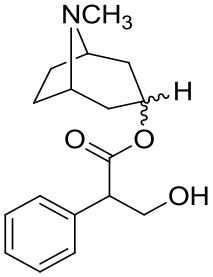


F
tropic acid ($C_9H_{10}O_3$)



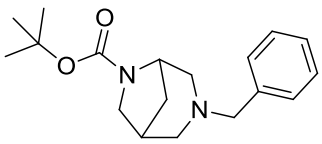
G

27.3

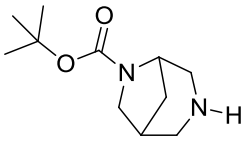


H: atropine

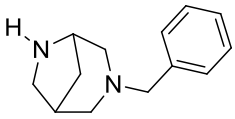
27.4



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



J

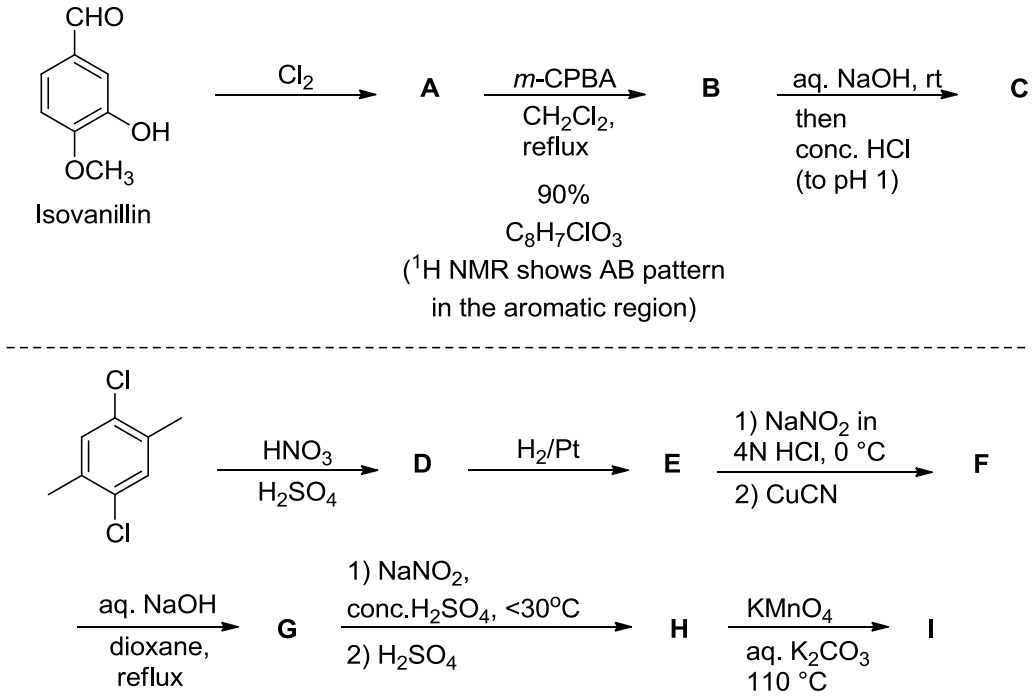


K

THEORETICAL PROBLEM 28

Synthesis of Building Blocks for Fluorescent Markers

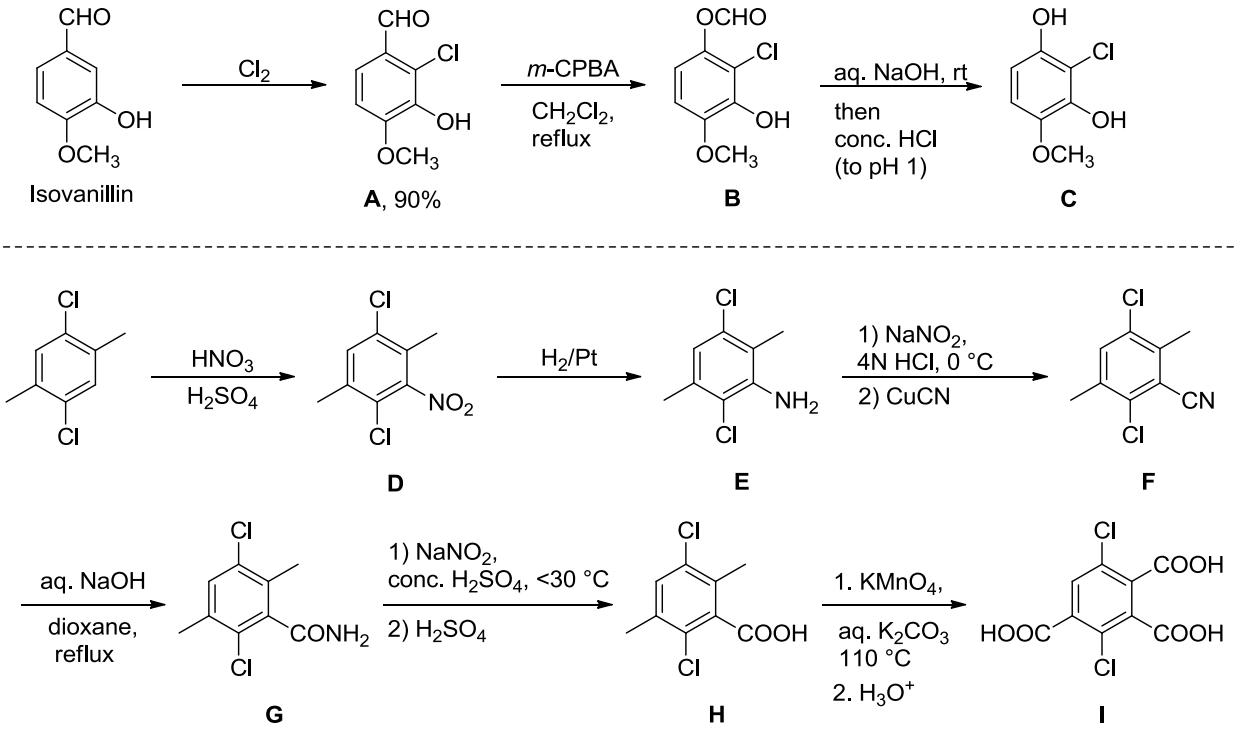
Carboxy-functionalized fluorescein dyes, which have been employed as important conjugated fluorescent markers of biologically active compounds, can be synthesized based on the improved synthetic route developed by M.H. Lyttle and co-workers (Lyttle, M. H.; Carter, T. G.; and Cook, R. M. *Org. Proc. Res. Dev.* **2001**, *5*, 45 – 49). In these synthetic sequences, two different precursors (**C** and **I**) were required and they were synthesized as followed.



28.1 Identify compounds **A**-**I**.

SOLUTION OF PREPARATORY PROBLEM 28

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

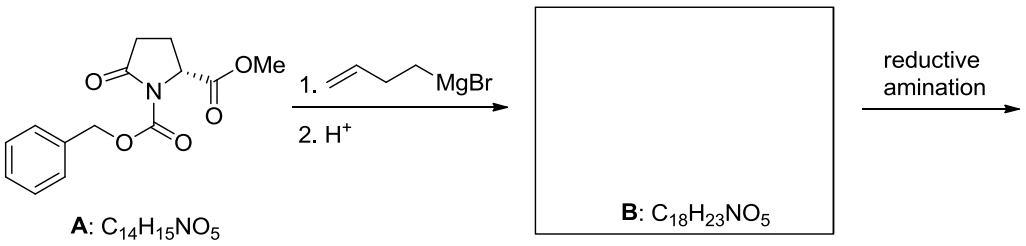


THEORETICAL PROBLEM 29

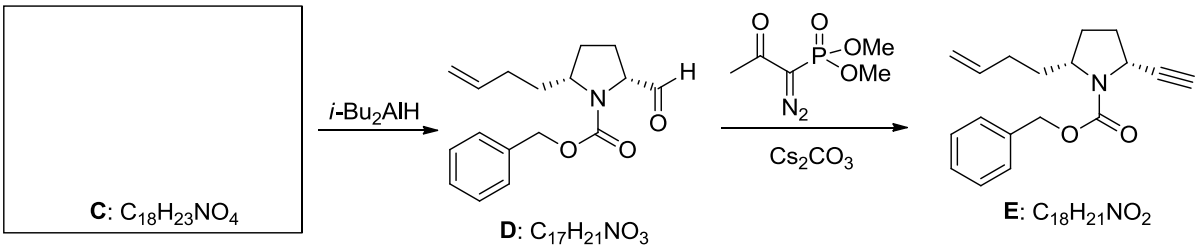
Synthesis towards Anatoxin-a

Anatoxin-a (**I**) is a secondary amine alkaloid with acute neurotoxicity that can cause death by respiratory paralysis. This compound is produced by several different genera of cyanobacteria found all over the world. In 2004, Jehrod B. Brenneman and Stephen F. Martin reported a concise synthesis of anatoxin-a from commercially available D-methyl pyroglutamate, which was converted to compound **A**.

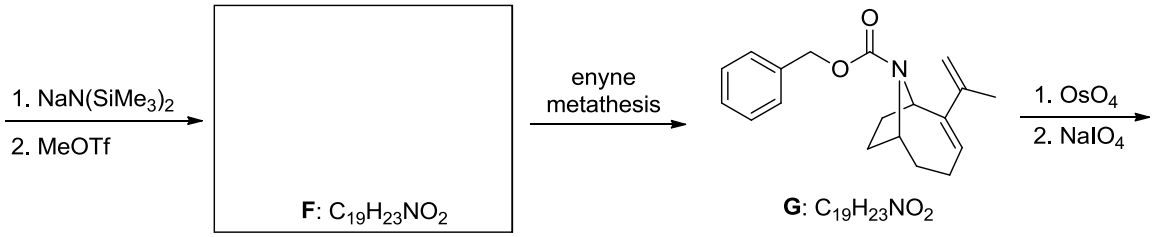
29.1 Write down the structural formulae of compounds **B**, **C**, **F**, **H** and **I** in the boxes provided.



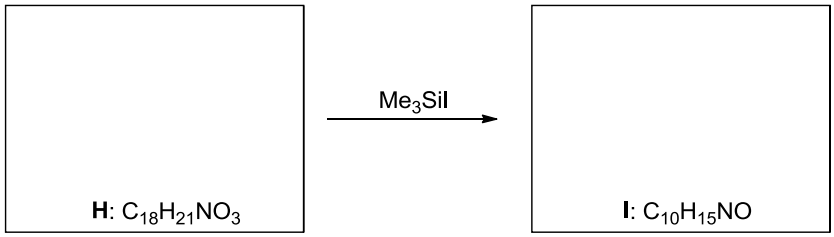
A: $C_{14}H_{15}NO_5$ **B**: $C_{18}H_{23}NO_5$



C: $C_{18}H_{23}NO_4$ **D**: $C_{17}H_{21}NO_3$ **E**: $C_{18}H_{21}NO_2$



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

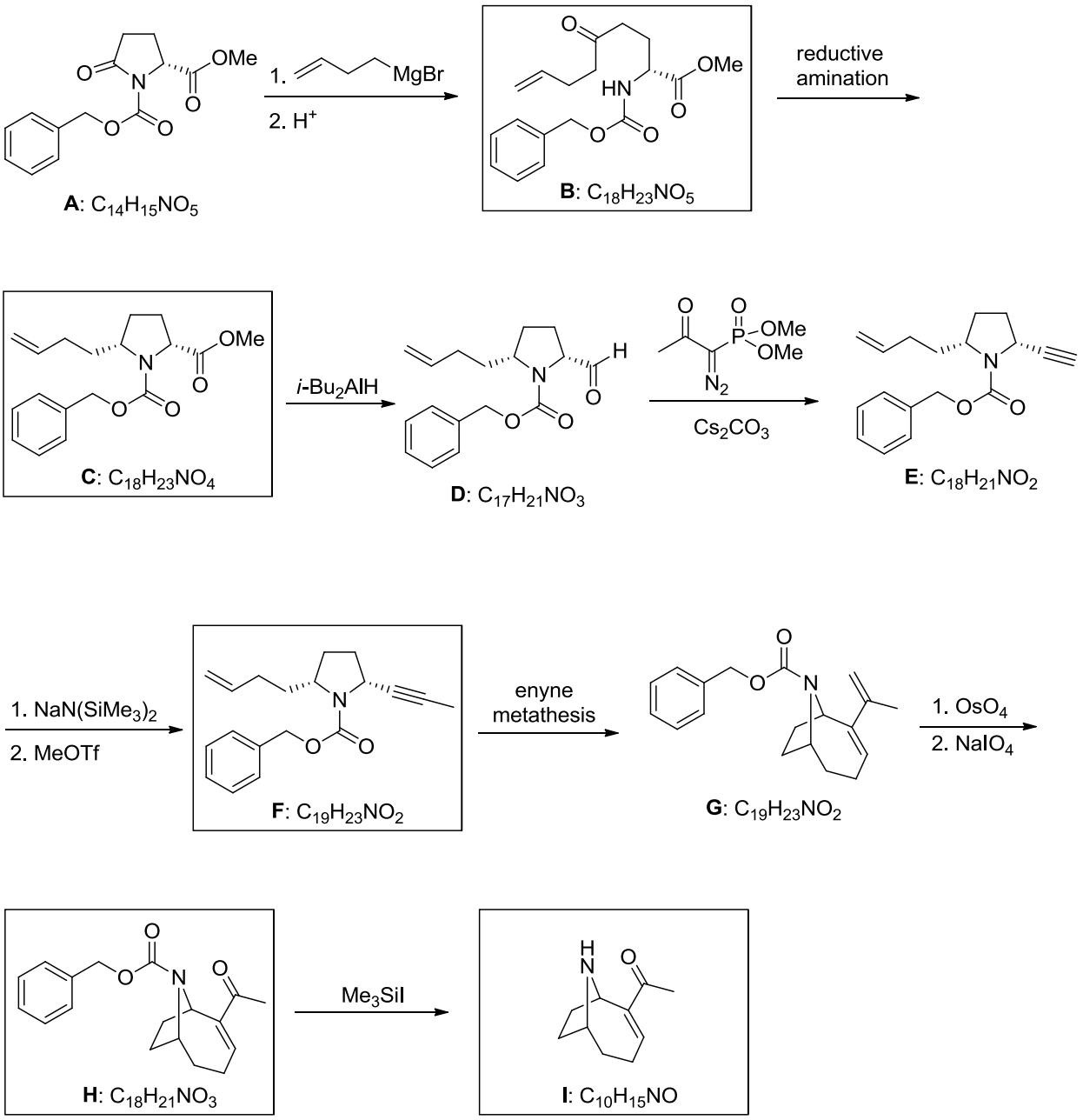


H: $C_{18}H_{21}NO_3$ **I**: $C_{10}H_{15}NO$

IR: (functional group region) 3392, 2933, 1663 cm^{-1}

SOLUTION OF PREPARATORY PROBLEM 29

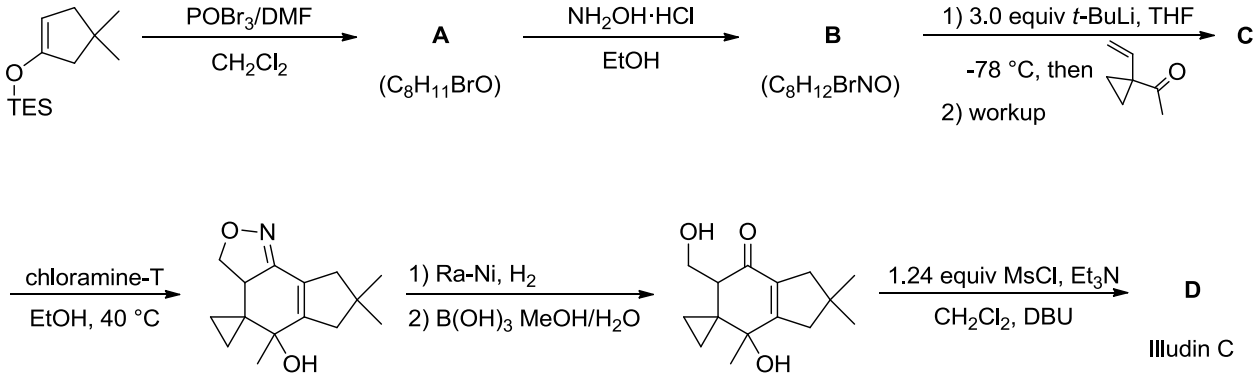
29.1



THEORETICAL PROBLEM 30

Total Synthesis of Illudin C

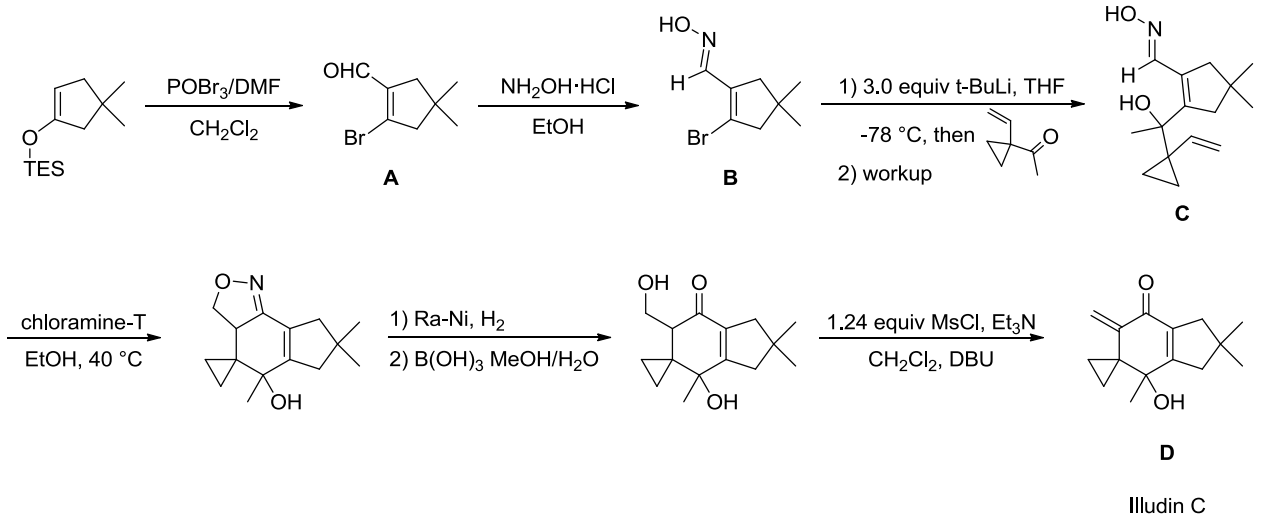
During the synthesis of sesquiterpene (±)-illudin C, R. L. Funk required the building block **C** which could be prepared based on the short synthesis shown below (Aungst Jr., R. A., Chan C., Funk R. L., *Org. Lett.* **2001**, *3*, 2611–2613.) Compound **C** was then carried on in the synthesis as shown.



30.1 Provide the correct structures of **A**, **B**, **C** and **D**.

SOLUTION OF PREPARATORY PROBLEM 30

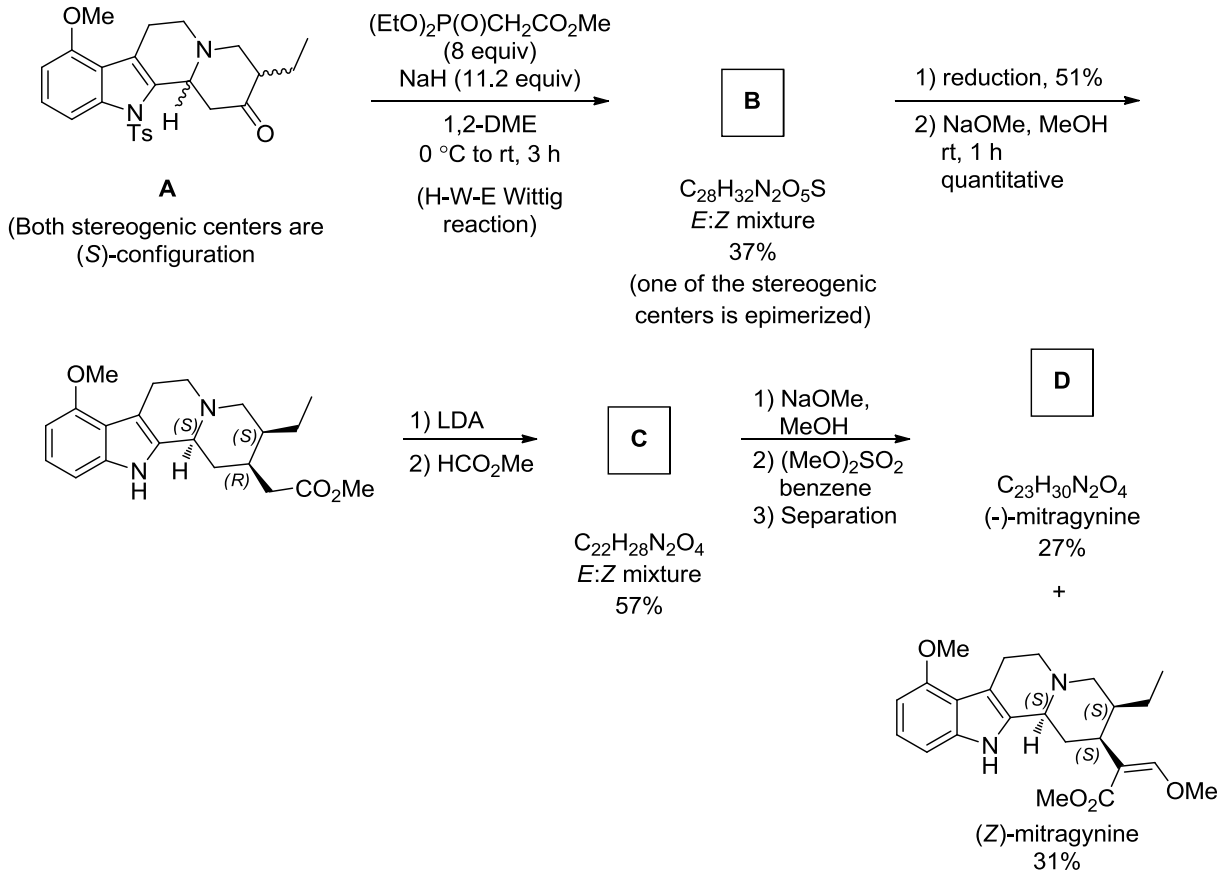
30.1 The structures of **A**, **B**, **C** and **D**:



THEORETICAL PROBLEM 31

Total Synthesis of μ-Opioid Receptor (MOR) Agonists

In the studies of pain management, μ-opioid receptor has been an important protein target in the central nervous system which interacts with specific small molecules and may therefore alleviate pain in patients. In studying this target, one needs to have access to these compounds. Nature has been a major source of these small compounds which may be used in the research. In addition to the parent compounds in plants which are known to reduce pain, synthetic derivatives are also equally important for the study. In a recent pharmacological evaluation of the synthetic mitragynine and derivatives, the principle alkaloids found in the Southeast Asian plant *Mitragyna speciosa* (known as Kratom in Thailand), by Sames and co-workers (Kruegel A. C. Gassaway M. M., Kapoor A., Váradi A., Majumdar S., Filizola M., Javitch J. A. and Sames D., *J. Am. Chem. Soc.* **2016**, *138*, 6754–6764), the materials for the evaluation were accessed *via* total synthesis. The brief synthesis is illustrated in the scheme below.

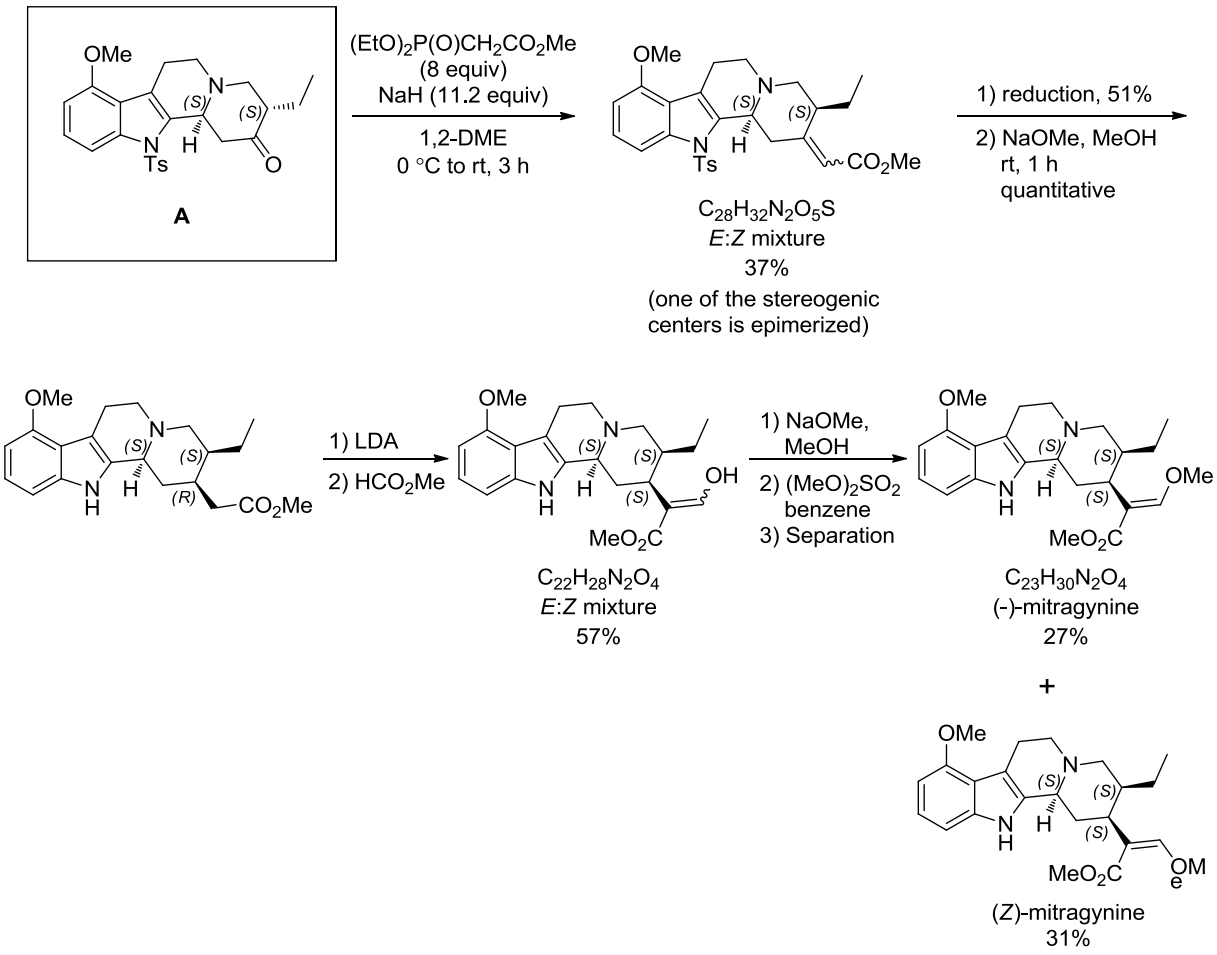


31.1 Draw the correct structure of compound **A**.

31.2 Identify the structures of compounds **B**-**D** with correct stereochemistry.

SOLUTION OF PREPARATORY PROBLEM 31

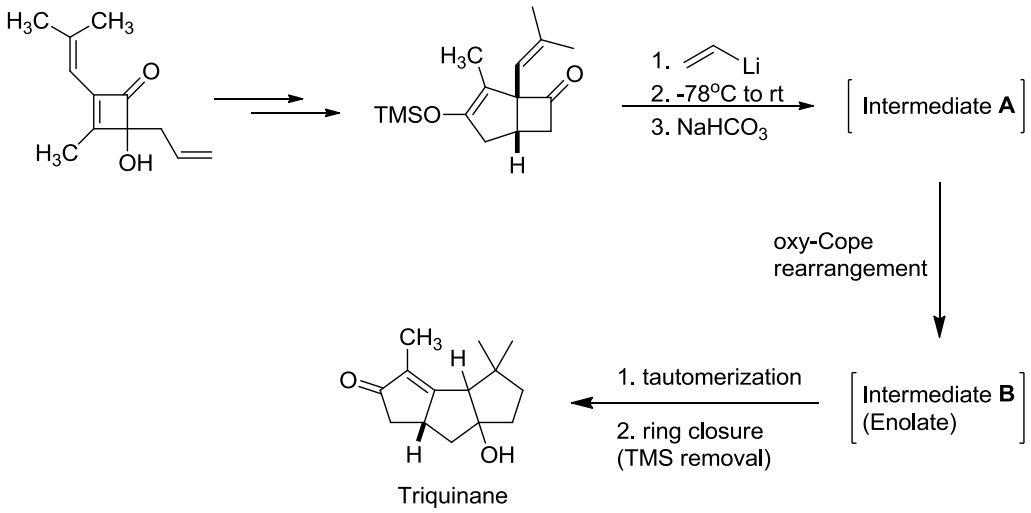
31.1



THEORETICAL PROBLEM 32

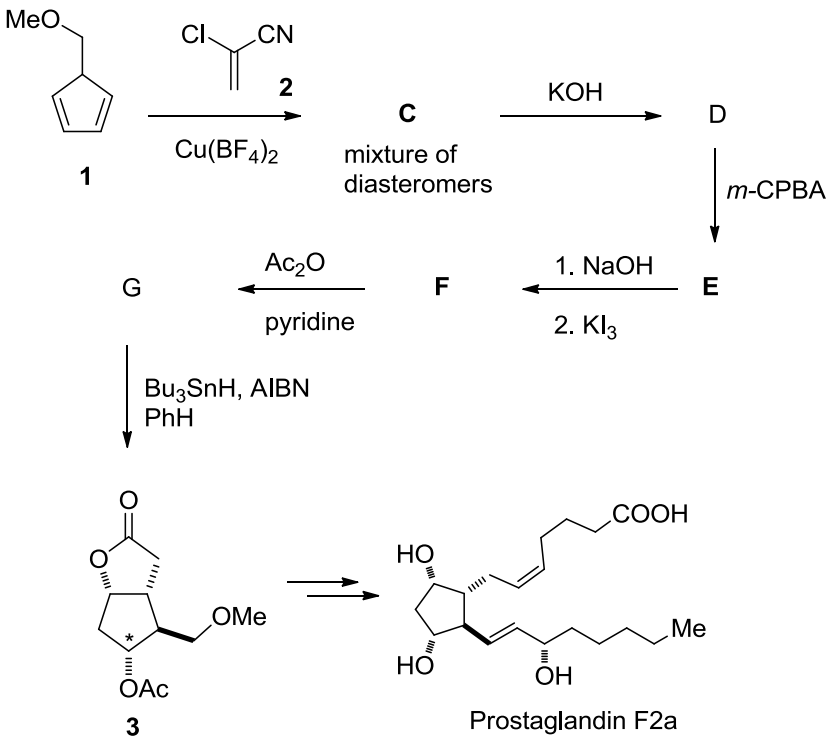
Pericyclic Reaction

A series of pericyclic reaction can be used to construct complex organic molecular structure in a stereocontrolled manner. For example, Moore *et al.* (*J. Org. Chem.* **1998**, *63*, 6905.) reported the synthesis of triquinane derivatives from the corresponding cyclobutenone as shown in scheme below.



32.1 Propose structures of intermediates **A** and **B**.

In the synthesis of prostaglandin, Corey *et al.* (*J. Am. Chem. Soc.* **1969**, *91*, 5675.) used cycloaddition reaction as a key step along with a series of straightforward chemical transformations to set up stereochemistry at the periphery of cyclopentyl structure as shown in scheme below.

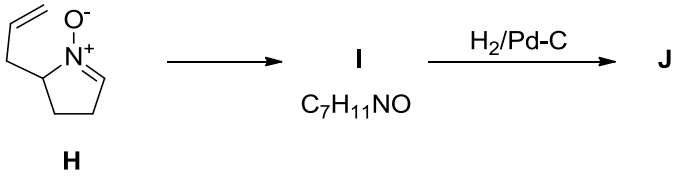


32.2 (i) Identify structures of compounds **C**-**G** with correct relative stereochemistry.

(ii) There is a carbon, labeled with an asterisk in compound **3**. Indicate the position of this labeled carbon in either compound **1** or **2** by placing an asterisk on the carbon in the given structure.

(iii) If a student synthesizes compound **3** from compounds **1** and **2** by following the synthetic scheme above, how many possible stereoisomers of compound **3** can the student obtain?

1,3-Dipolar cycloaddition is a powerful tool for the construction of heterocyclic structure. For example, upon heating, compound **H** undergoes intramolecular [4+2]-cycloaddition to yield compound **I**. Reduction of a weak N-O bond of compound **I** by catalytic hydrogenation gave product **J**.

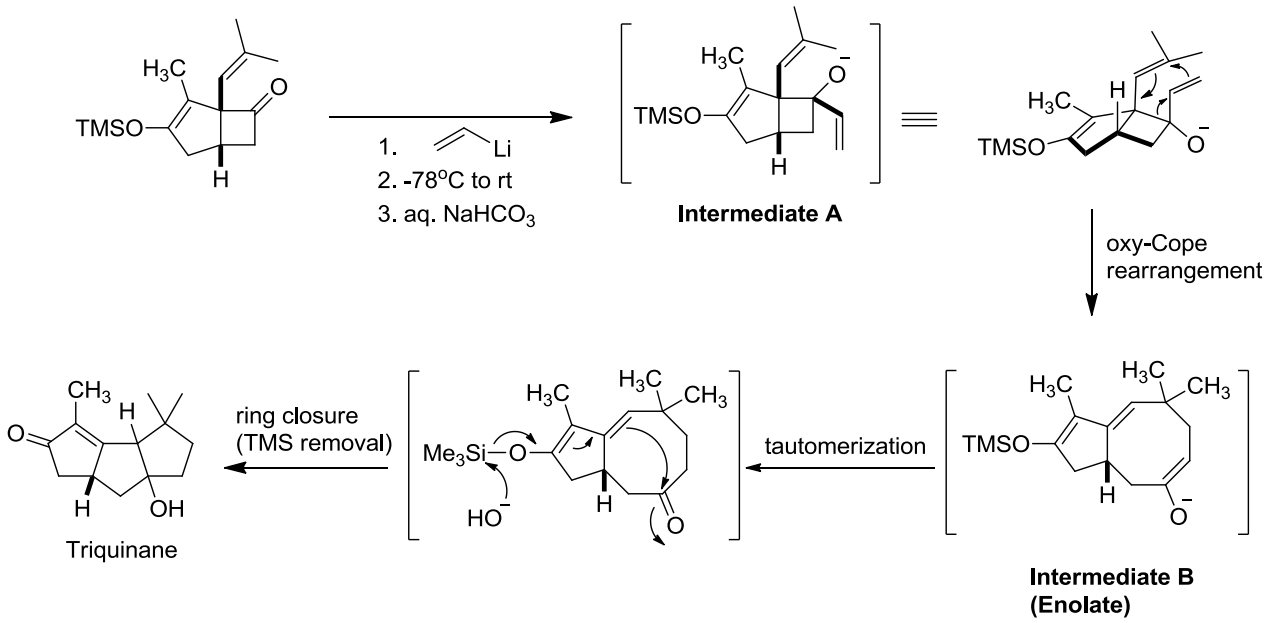


32.3 (i) Propose structures of compounds **I** and **J**.

(ii) If a racemic mixture of **H** is used in the reaction, write all possible stereo-isomer(s) of products **J**.

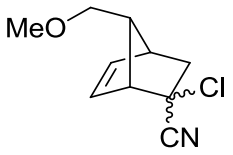
SOLUTION OF PREPARATORY PROBLEM 32

32.1

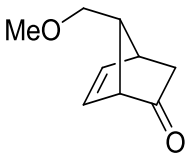


32.2

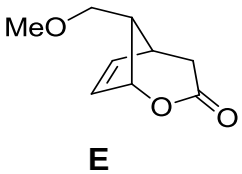
(i) Structures of compounds **C** - **G**



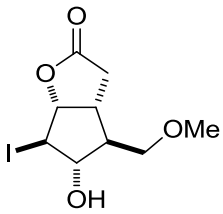
C



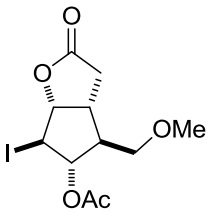
D



E

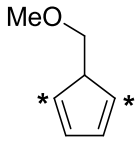


F

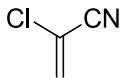


G

(ii)



1



2

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

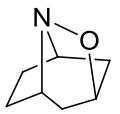
(iii) Two.

Reaction between **1** and **2** will give a pair of enantiomers which are inseparable.

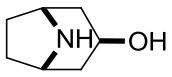
(Note: The two enantiomers can be resolved but this process is not mentioned in the context.) The subsequent processes, although generated a few new chiral centers, employed achiral reagent and the newly formed stereocenters were controlled by the existing stereochemistry. Therefore, stereochemical information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

32.3

(i)



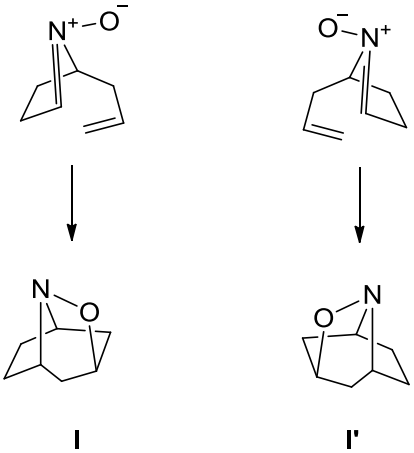
I



J

(ii) Racemic mixture of **H** will give product **I** which has a plane of symmetry.

Therefore, reduction of **I** (only a stereoisomer) will give only 1 possible product **J**.



I **I'**

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

THEORETICAL PROBLEM 33

Stereoisomers without stereocenter

Axial chirality refers to stereoisomerism of a special case of chirality in which a molecule does not possess a stereogenic center but an axis of chirality. An axis of chirality is defined as an axis about which a set of substituents is held in a spatial arrangement that is not superimposable on its mirror image.

Two necessary preconditions for axial chirality are:

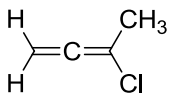
i. A rotationally stable axis

ii. Presence of different substituents on both sides of the axis

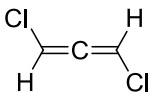
Axial chirality is most commonly observed in atropisomeric biaryl compounds wherein the rotation about the aryl-aryl bond is restricted, for example, biphenyl, binaphthyls. Certain allene compounds also display axial chirality.

33.1 From the given structures, draw 3-D structure and the corresponding mirror image of the given compounds. Use plane of symmetry to determine whether they are chiral or achiral.

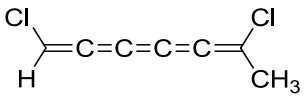
(i)



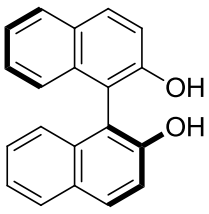
(ii)



(iii)

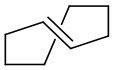


(iv)

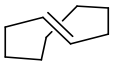


33.2 Enantiomers of medium ring *trans*-cycloalkenes exist. For example, *trans*-cyclooctene can be resolved and its enantiomers are stable at room temperature. On the other hand, *trans*-cyclononene has also been resolved but it racemizes with a half-life of 4 min. at 0°C.

(i) Draw mirror images of the given structures of *trans*-cyclooctene and *trans*-cyclononene.



trans-cyclooctene



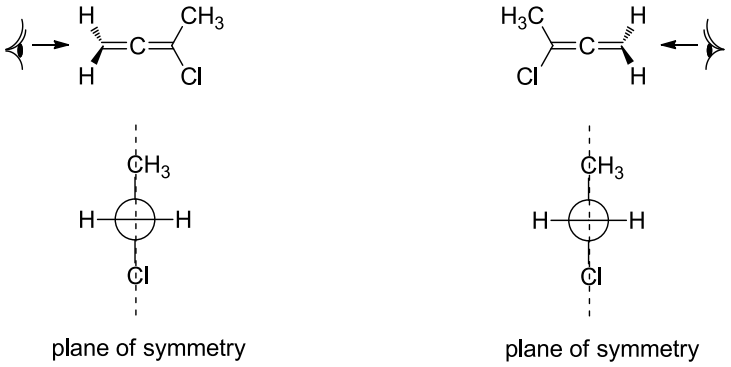
trans-cyclononene

(ii) Why does *trans*-cyclononone racemize faster than *trans*-cyclooctene?

SOLUTION OF PREPARATORY PROBLEM 33

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

33.1 (i) From the possible enantiomeric pair,

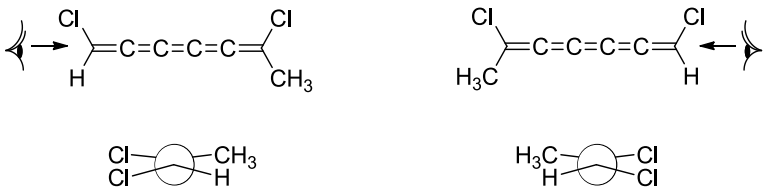


The molecule has a plane of symmetry, therefore, the structure is achiral.

(ii) From the possible enantiomeric pair,

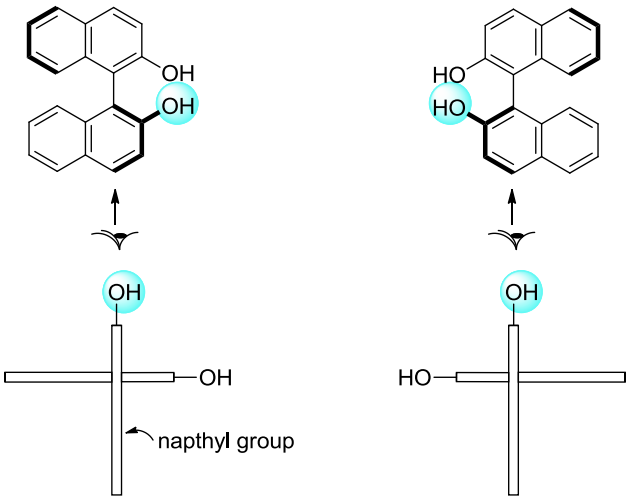
There is no plane of symmetry in these two molecules. Therefore, these two mirror image structures are non-superimposable. The structure is chiral.

(iii) From the structure of cumulene,



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

(iv) From the possible enantiomeric pair,



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

33.2 (i)

trans-cyclooctene *trans*-cyclononene

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

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

PRACTICAL PROBLEMS

PRACTICAL PROBLEM 1P

Quantitative Determination of Ascorbic Acid and Citric Acid in Beverages

The weather in Thailand is generally hot and humid which may cause discomfort and fatigue. Therefore drinking of water or beverage is optional choice to refresh and reduce an appetite. There are various brands of drink available in the markets. The main components in the beverage are sweetener, organic acid, minerals as well as color and flavor. These components basically improve the taste and texture.

In this task, you will determine the amount of ascorbic acid ($C_6H_8O_6$) and citric acid ($C_3H_5O(COOH)_3$) that are in a beverage sample by two titrations.

A) Determination of ascorbic acid by redox titration

B) Determination of *total acid* content by acid-base titration

Source: Sigmann S. B. and Wheeler D. E., *J. Chem. Educ.*, **2004**, *81*, 1479.

Chemicals

- KIO_3 solution, (c = 0.001 mol dm^{-3})
- HCl solution, (c = 1 mol dm^{-3})
- starch solution, 0.5 % w/v
- NaOH solution*)
- phenolphthalein indicator, 0.5 % w/w
- KI
- Sample (solution containing ascorbic acid (c = 1.28×10^{-3} mol dm^{-3}) and citric acid (c = 6.76×10^{-2} mol dm^{-3})

___

*) This solution must be standardized. Use potassium hydrogen phthalate (KHP) for the standardization.

Glasswares

- Burets
- volumetric pipet, 50 cm^3

- volumetric pipet, 10 cm^3
- pipet bulb
- 6 Erlenmeyer flasks

A) Determination of ascorbic acid by redox titration

The amount of ascorbic acid is determined by titration with KIO_3. The reaction equations are shown as equations (1) – (4).

$$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O \quad (1)$$

$$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2\ H^+ + 2\ I^- \quad (2)$$

$$I_2 + I^- \rightarrow I_3^- \quad (3)$$

$$I_3^- + \text{starch} \rightarrow \text{starch - } I_3^- \text{ complex} \quad (4)$$

(blue)

Procedure

1. Fill a buret with a KIO_3 solution, (c = 0.001 mol dm^{-3})
2. Pipet a 50.00 cm^3 aliquot of the sample solution and quantitatively transfer it to an Erlenmeyer flask. Add 1 gram of KI, 5 cm^3 of HCl solution (c = 1 mol dm^{-3}) and 3 cm^3 of 0.5 % starch solution to the flask.
3. Titrate with KIO_3 solution (0.001 mol dm^{-3}) immediately.
4. Endpoint is marked by the appearance of the blue starch–I_3^-complex.
5. Repeat with two additional 50.00 cm^3 aliquots.

(i) Fill the data in the Table.

Titration No.	**1**	**2**	**3**
Initial reading of the burette, cm^3			
Final reading of the burette, cm^3			
Consumed KIO_3 volume, cm^3			

(ii) Calculate the mass of ascorbic acid (in mg) per 100 cm^3 of sample.

B) Determination of *total acid* content by acid-base titration

Procedure

1. Pipet a 10.00 cm^3 aliquot of the sample solution and quantitatively transfer it to Erlenmeyer flask.
2. Add 2-3 drops of phenolphthalein indicator to the flask.
3. Slowly add NaOH solution from the buret to the flask.
4. At the endpoint, color of the indicator will change from colorless to pink.
5. Repeat the titration with two additional 10.00 cm^3 aliquots.

Titration with NaOH therefore determines the amount of *total acid* in the sample. The equations of the reactions are shown as equations (5) and (6).

$$C_6H_8O_6 + NaOH \rightarrow C_6H_7O_6Na + H_2O \quad (5)$$

$$C_3H_5O(COOH)_3 + 3\ NaOH \rightarrow C_3H_5O(COO)_3Na_3 + 3\ H_2O \quad (6)$$

(i) Fill the Table below

Titration no.	**1**	**2**	**3**
Initial reading of the buret, cm^3			
Final reading of the buret, cm^3			
Consumed base volume, cm^3			

(ii) Calculate the amount of substance of the reacted hydroxide (in moles)

The amount of citric acid is determined by the difference as shown below.

n(NaOH) neutralized (total acid) - moles NaOH neutralized (ascorbic acid) =

= moles NaOH neutralized (citric acid)

(iii) Calculate the mass of citric acid (in grams) per 100 cm^3 of sample

PRACTICAL PROBLEM 2P

Spectrophotometric Determination of Chromium and Manganese

According to Beer's law, the net absorbance is an additive of each solute, provided there is no reaction between the two solutes.

$A^{\lambda_1}_{total} = A^{\lambda_1}_X + A^{\lambda_1}_Y$

$A^{\lambda_2}_{total} = A^{\lambda_2}_X + A^{\lambda_2}_Y$

where A_{total} are the net measured absorbances at λ_1 and λ_2 respectively, and A_X and A_Y are the absorbances of the two solutes.

Chemicals

Solutions:

- H_2SO_4, $c =$ 0.5 mol dm^{-3}
- $KMnO_4$, $c =$ 0.01 mol dm^{-3}
- $K_2Cr_2O_7$, $c =$ 0.01 mol dm^{-3}

Instrument

Visible spectrophotometer

Glasswares

- 2 measuring pipets, 2.00 cm^3
- 2 measuring pipets, 10.00 cm^3
- 13 volumetric flasks, 50.00 cm^3
- pipet bulb

A) Determination of molar absorption coefficients of $KMnO_4$ and $K_2Cr_2O_7$

1. Prepare four standard $KMnO_4$ solutions with a concentration of 0.5×10^{-4}, 1.0×10^{-4}, 2.0×10^{-4}, and 5.0×10^{-4} mol dm^{-3}, respectively, in 0.5 mol dm^{-3} H_2SO_4 by appropriate dilution from standard 0.01mol dm^{-3} $KMnO_4$ solution to the final volume of 50.00 cm^3 in volumetric flask.
2. Prepare standard $K_2Cr_2O_7$ solutions of 2.0×10^{-4}, 3.0×10^{-4}, 4.0×10^{-4}, 6.0×10^{-4} mol dm^{-3} in 0.5 mol dm^{-3} H_2SO_4 by appropriate dilution from standard 0.01 mol dm^{-3} $K_2Cr_2O_7$ solution to the final volume of 50.00 cm^3 in volumetric flask.

3. Record the absorbance values of all solutions at 440 and 545 nm.

Concentration of $KMnO_4$ (mol dm^{-3})	Absorbance (*A*) (at 440 nm)	Absorbance (*A*) (at 545 nm)	Molar absorption coefficient (at 440 nm)	Molar absorption coefficient (at 545 nm)
0.5×10^{-4}				
1.0×10^{-4}				
2.0×10^{-4}				
5.0×10^{-4}				
Molar absorption coefficient (average)				

Concentration of $K_2Cr_2O_7$ (mol dm^{-3})	Absorbance (A) (at 440 nm)	Absorbance (A) (at 545 nm)	Molar absorption coefficient (at 440 nm)	Molar absorption coefficient (at 545 nm)
2.0×10^{-4}				
3.0×10^{-4}				
4.0×10^{-4}				
6.0×10^{-4}				
Molar absorption coefficient (average)				

B) Determination the concentrations of $KMnO_4$ and $K_2Cr_2O_7$ in solution mixture

1. Prepare a solution using 5.0 cm^3 of $KMnO_4$ solution ($c = 0.5\times10^{-4}$ mol dm^{-3}) and 5.0 cm^3 of $K_2Cr_2O_7$ solution ($c = 6.0\times10^{-4}$ mol dm^{-3}) (Solution A).
2. Prepare a solution using 5.0 cm^3 of $KMnO_4$ solution ($c = 2.5\times10^{-4}$ mol dm^{-3}) and 5.0 cm^3 of $K_2Cr_2O_7$ solution ($c = 4.0\times10^{-4}$ mol dm^{-3}) (Solution B)
3. Prepare a solution using 5.0 cm^3 of $KMnO_4$ solution ($c = 5.0\times10^{-4}$ mol dm^{-3}) and 5.0 cm^3 of $K_2Cr_2O_7$ solution ($c = 2.0\times10^{-4}$ mol dm^{-3}) (Solution C)
4. Record the absorbance values of all solutions at 440 and 545 nm

Solution	Absorbance (*A*) (at 440 nm)	Absorbance (*A*) (at 545 nm)
A		
B		
C		

Calculate the concentration of $KMnO_4$ and $K_2Cr_2O_7$ in each solution (from the experimental absorbance values)

Solution	$KMnO_4$ (mol dm^{-3})	% error	$K_2Cr_2O_7$ (mol dm^{-3})	% error
A				
B				
C				

PRACTICAL PROBLEM P3

Synthesis of "Ferrocenated" Iron Oxide Nanoparticles and Their Activities in the Decolorization of Methylene Blue

Ferrocenated compounds are a mixture containing ferrocene, iron oxide, and cyclopentadienyl radical. The preparation of ferrocenated compounds can be done by the decomposition of ferrocenium in basic condition. Cyclopentadienyl radical in ferrocenated compounds is an active specie to generate reactive oxygen species for the decolorization of methylene blue.

In this task, you will:

a) Perform the synthesis of ferrocenated iron oxide nanoparticles by coprecipitation.
b) Perform the decolorization of methylene blue by ferrocenated iron oxide, and follow reaction by spectrophotometric analysis.

Chemicals

Ferric chloride hexahydrate ($FeCl_3 \cdot 6\ H_2O$)	De-ionized water
Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4\ H_2O$)	Sodium hydroxide
Ferrocene	Barium chloride
Concentrated sulfuric acid	Methylene blue

Glasswares

- Round-bottomed flask, 250 cm^3
- Beaker, 25 cm^3
- Beaker, 100 cm^3
- Beaker, 250 cm^3
- Erlenmeyer flask, 250 cm^3
- Volumetric flask, 250 cm^3
- Graduated cylinder, 10 cm^3
- Graduated cylinder, 100 cm^3
- Test tubes
- Pasteur pipets and rubber bulb
- Magnetic bars
- Stirring rods

- Evaporation dish
- Centrifuge tubes
- Aluminum foil

Instruments

- Stirrer
- 4-digit balance
- pH meter
- Centrifuge
- Oven
- Visible Spectrophotometer

Synthesis of ferrocenated iron oxide nanoparticles

1. Add concentrated sulfuric acid (0.5 cm^3) to ferrocene (6.84 g) to yield a ferrocenium solution. Do this experiment in a fume hood.
2. Add the ferrocenium solution to water (5 cm^3) and stir for 30 minutes.
3. Prepare a mixed solution of ferrous chloride tetrahydrate (1.55 g) and ferric chloride hexahydrate (4.15 g) in de-ionized water (80 cm^3).
4. Add the mixed solution into the blue solution of ferrocenium and then stir for 1 hour.
5. Add a saturated NaOH solution slowly until the pH of solution is 12.
6. Collect the orange precipitate by centrifugation at 4500 rpm for 20 minutes.
7. Wash the precipitate with de-ionized water. Be sure that sulfate ion is completely washed by checking with $BaCl_2$ solution.
8. Dry orange solid at 100 °C for 1 hour. Record the weight and calculate the yield of the ferrocenated iron oxide.

Decolorization of methylene blue

1. Prepare a solution of methylene blue (9.97×10^{-6} mol dm^{-3}).
2. Add 100 cm^3 of methylene blue in a 250 cm^3-Erlenmeyer flask which is wrapped with aluminum foil. Keep this flask in a dark box while stirring.
3. Add the prepared orange solid (0.100 g) into the solution of methylene blue.
4. Collect 3 cm^3 of the mixture at every 5 minutes.

5. Centrifuge the mixture at 4500 rpm for 3 minutes.
6. Take the clear supernatant for spectrophotometric analysis.

Plot a graph between the absorbance at a specific wavelength and reaction time.

You may prepare iron oxide by repeating the above experiments without the addition ferrocene and perform the decolorization of methylene blue for comparison with ferrocenated iron oxide.

PRACTICAL PROBLEM P4

Synthesis of Aspirin

Aspirin or acetylsalicylic acid (ASA) is a well-known medication for the treatment of pain, fever, and inflammation. It is a nonsteroidal anti-inflammatory drug (NSAID). Aspirin irreversibly inhibits COX enzyme results in the decrease in the production of prostaglandins and thromboxanes, the key molecules that affect various physiological responses including transmission of pain, regulation of inflammation and fever, as well as aggregation of platelets.

In this task, you will:

a) Perform the synthesis of acetylsalicylic acid *via* the esterification of salicylic acid with acetic anhydride.

b) Calculate % yield of the purified product.

c) Perform thin layer chromatography analysis.

Chemicals

- Acetic anhydride
- Salicylic acid
- Ethyl acetate
- Concentrated H_2SO_4 (18 mol dm^{-3})
- Hexane
- Ethanol
- Distilled Water

Glasswares

- Beaker, 100 cm^3
- Buchner funnel
- Crystallizing dish (for a hot water bath and an ice bath)
- Erlenmeyer flasks, 125 cm^3 and 250 cm^3
- Filter paper
- Graduated cylinder, 25 cm^3
- Pasteur pipet and rubber bulb
- Stirring rod
- Spatula

- Suction flask
- Capillary tube for TLC
- TLC plate on aluminum foil or glass supports and TLC jar

Instruments

- Analytical balance (± 0.0001 g)
- Hotplate
- Water aspirator or vacuum pump
- Stand and clamps

Procedure:

1. Weigh out 5.00 g of salicylic acid. Transfer this to a 125 cm^3 Erlenmeyer flask. Record the mass.
2. In the hood, add 7.0 cm^3 of acetic anhydride to the flask contained salicylic acid.
3. Carefully add 8 drops of concentrated sulfuric acid (18 mol dm^{-3}) to the reaction flask.
4. Assemble a hot water bath using a beaker and a hotplate.
5. Place the flask in the water bath and heat. After the water begins to boil, heat for an additional 15 minutes.
6. Allow the reaction flask to cool down for few minutes.
7. Carefully add 15.0 cm^3 of room temperature water to the flask. Swirl the flask to mix the contents.
8. Place the reaction flask in an ice bath. Let it cool down until the crystallization of the product completes (approx. 15 minutes). If crystals do not appear, scratch the walls of the flask with a stirring rod to induce crystallization.
9. Collect the solid product by vacuum filtration using a Buchner funnel.
10. Transfer the solid product from the Buchner funnel to a 250 cm^3 Erlenmeyer flask. Recrystallize the crude product with ethanol and water.

Recrystallization Protocol: Add preheated ethanol until the product is all dissolved. While heating the solution, add water dropwise and swirl. Keep adding water until the solution becomes cloudy. To the cloudy solution, hot ethanol is added dropwise until the solution becomes clear. Remove the flask from heating and allow the solution to cool

down undisturbed to the room temperature. Crystals should form. Chill the flask containing crystals in an ice-water bath to complete crystallization.

11. Collect the crystalline product using by vacuum filtration using a Buchner funnel.
12. Dry the product. Record weight and determine % yield
13. Perform thin layer chromatography (TLC) to determine the purity of the purified product.

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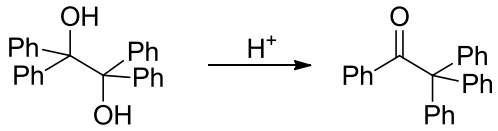
PRACTICAL PROBLEM P5

Synthesis of Benzopinacolone

The pinacol–pinacolone rearrangement can be used to convert 1,2-diol to carbonyl compound. The reaction takes place under acidic conditions. In this experiment, benzopinacol could be transformed to benzopinacolone *via* acid-catalyzed carbocation rearrangement.



In this task, you will:

a) Perform the acid catalyzed pinacol–pinacolone rearrangement.

b) Calculate % yield of the purified product.

Chemicals

- Benzopinacol
- Ethyl acetate
- Glacial acetic acid
- Hexane
- Iodine
- Ice (for an ice bath)
- Silicone oil or alike for oil bath

Glasswares

- Beaker, 600 cm^3
- Round-bottomed flask, 100 cm^3
- Erlenmeyer flask, 125 cm^3
- Suction flask
- Buchner funnel
- Reflux condenser
- Pasteur pipette and rubber bulb
- Stirring rod
- Graduated cylinder, 25 cm^3

- Filter paper
- Ice bath
- Oil bath
- Spatula
- Magnetic bar or boiling chip

Instruments

- Analytical balance (± 0.0001 g)
- Hotplate stirrer
- Water aspirator or vacuum pump
- Stand and clamps

Procedure:

1. Place 25 cm^3 of glacial acetic acid and 0.1 g of iodine in a 100 cm^3 round-bottomed flask equipped with a reflux condenser.
2. Add 0.015 mol of benzopinacol. (Benzopinacol could be prepared from photochemical reaction of benzophenone and isopropyl alcohol, see **appendix C**.)
3. Reflux the solution for 10 minutes in a hot oil bath.
4. Cool the reaction mixture to room temperature.
5. Collect the solid by vacuum filtration using Buchner funnel. Record the mass of crude product.
6. Recrystallize the crude product with the mixture of ethyl acetate and hexane (*The recrystallization protocol is similar to that described in* ***Task P4***).
7. Collect the crystals by vacuum filtration using Buchner funnel. Record the mass of recrystallized product.
8. Determine the yield of the product.