# 35th

ICHO

International Chemistry Olympiad

**35 theoretical problems**
**2 practical problems**

# THE THIRTY-FIFTH
## INTERNATIONAL CHEMISTRY OLYMPIAD
## 5–14 JULY 2003, ATHENS, GREECE

# THEORETICAL PROBLEMS

## SECTION A: General Chemistry

### QUESTION 1

The molar solubility *s* (mol $dm^{-3}$) of $Th(IO_3)_4$ as a function of the solubility product $K_{sp}$ of this sparingly soluble thorium salt is given by the equation:

(a) $s = (K_{sp} / 128)^{1/4}$ ( )

(b) $s = (K_{sp} / 256)^{1/5}$ ( )

(c) $s = 256\ K_{sp}^{1/4}$ ( )

(d) $s = (128\ K_{sp})^{1/4}$ ( )

(e) $s = (256\ K_{sp})^{1/5}$ ( )

(f) $s = (K_{sp} / 128)^{1/5} / 2$ ( )

### QUESTION 2

Which one of the following equations must be used for the exact calculation of $[H^+]$ of an aqueous HCl solution at any concentration $c_{HCl}$? ($K_w = 1\times10^{-14}$).

(a) $[H^+] = c_{HCl}$ ( )

(b) $[H^+] = c_{HCl} + K_w / [H^+]$ ( )

(c) $[H^+] = c_{HCl} + K_w$ ( )

(d) $[H^+] = c_{HCl} - K_w / [H^+]$ ( )

### QUESTION 3

The molar mass of glucose ($C_6H_{12}O_6$) is 180 g $mol^{-1}$ and $N_A$ is the Avogadro constant. Which <u>one</u> of the following statements <u>is not correct</u>?

(a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 $cm^3$ of solution. ( )

(b) 1.00 mmol amount of glucose has a mass of 180 mg. ( )

(c) 0.0100 mol of glucose comprises of $0.0100 \times 24 \times N_A$ atoms. ( )

(d) 90.0 g glucose contain $3 \times N_A$ atoms of carbon. ( )

(e) 100 $cm^3$ of a 0.10 M solution contain 18 g of glucose. ( )

## QUESTION 4

If the density of a liquid compound B is $\rho$ (in g $cm^{-3}$), $M$ is the molar mass of B and $N_A$ is the Avogadro constant, then the number of molecules of B in 1 $dm^3$ of this compound is:

(a) $(1000 \times \rho) / (M \times N_A)$ ( )

(b) $(1000 \times \rho \times N_A) / M$ ( )

(c) $(N_A \times \rho) / (M \times 1000)$ ( )

(d) $(N_A \times \rho \times M) / 1000$ ( )

## QUESTION 5

The equilibrium constant of the reaction:

$Ag_2CrO_4(s) + 2\ Cl(aq)^- \rightleftharpoons 2\ AgCl(s) + CrO_4^{2-}(aq)$

is given by the equation:

(a) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)^2$ ( )

(b) $K = K_{sp}(Ag_2CrO_4) \times K_{sp}(AgCl)^2$ ( )

(c) $K = K_{sp}(AgCl) / K_{sp}(Ag_2CrO_4)$ ( )

(d) $K = K_{sp}(AgCl)^2 / K_{sp}(Ag_2CrO_4)$ ( )

(e) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)$ ( )

## QUESTION 6

How many $cm^3$ of 1.00 M NaOH solution must be added to 100.0 $cm^3$ of 0.100 M $H_3PO_4$ solution to obtain a phosphate buffer solution with *pH* of about 7.2? (The *pK* values for $H_3PO_4$ are $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

(a) 5.0 $cm^3$ ( )

(b) 10.0 $cm^3$ ( )

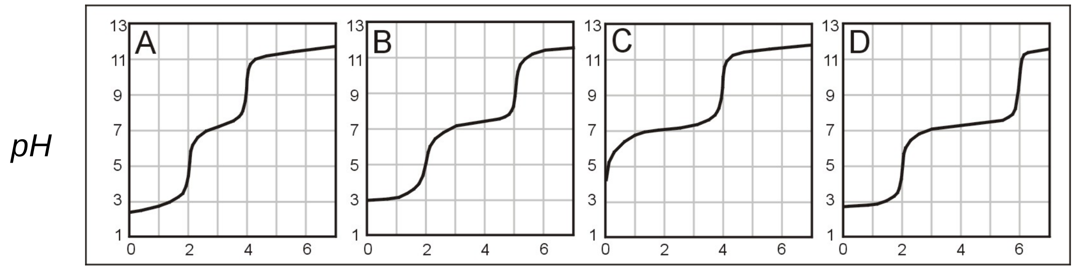
(c) 15.0 mL ( )

(d) 20.0 mL ( )

## QUESTION 7

Solutions containing $H_3PO_4$ and/or $NaH_2PO_4$ are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (*pH vs*. volume of titrant) shown in the figure:

(For $H_3PO_4$: $pK_1$ = 2.1, $pK_2$ = 7.2, $pK_3$ = 12.0)




Volume of titrant ($cm^3$)

a) The sample contains $H_3PO_4$ only.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) The sample contains both in a mole ratio $H_3PO_4$ : $NaH_2PO_4$ = 2 : 1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) The sample contains both in a mole ratio $H_3PO_4$ : $NaH_2PO_4$ = 1 : 1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

## QUESTION 8

A fuel/oxidant system consisting of N,N-dimethylhydrazine $(CH_3)_2NNH_2$ and $N_2O_4$ (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that $N_2$, $CO_2$ and $H_2O$ are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 1 mol of $(CH_3)_2NNH_2$?

(a) 8 ( )

(b) 9 ( )

(c) 10 ( )

(d) 11 ( )

(e) 12 ( )

## QUESTION 9

The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

(a) F ( )

(b) (4/3) F ( )

(c) (3/2) F ( )

(d) 2 F ( )

(e) 3 F ( )

## QUESTION 10

Identify particle X in each of the following nuclear reactions:

a) $^{68}_{30}Zn + ^{1}_{0}n \rightarrow ^{65}_{28}Ni + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

b) $^{130}_{52}Te + ^{2}_{1}H \rightarrow ^{131}_{53}I + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

c) $^{214}_{82}Pb \rightarrow ^{214}{}_{83}Bi + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

d) $^{23}_{11}Na + ^{1}_{0}n \rightarrow ^{24}_{11}Na + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

e) $^{19}_{9}F + ^{1}_{0}n \rightarrow ^{20}_{9}F + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

## QUESTION 11

10.0 cm$^3$ of 0.50 M HCl and 10.0 cm$^3$ of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of $\Delta T$ is recorded. Estimate the temperature increase if 5.0 cm$^3$ of 0.50 M NaOH were used instead of 10.0 cm$^3$. Thermal l osses are negligible and the specific heats of both solutions are taken as equal.

(a) (1/2) $\Delta T$ ( )

(b) (2/3) $\Delta T$ ( )

(c) (3/4) $\Delta T$ ( )

(d) $\Delta T$ ( )

## QUESTION 12

Natural antimony consists of the following 2 stable isotopes: $^{121}Sb$, $^{123}Sb$. Natural chlorine consists of the following 2 stable isotopes: $^{35}Cl$, $^{37}Cl$. Natural hydrogen consists of the following 2 stable isotopes: $^{1}H$, $^{2}H$. How many peaks are expected in a low resolution mass spectrum for the ionic fragment $SbHCl^{+}$?

(a) 4 ( )

(b) 5 ( )

(c) 6 ( )

(d) 7 ( )

(e) 8 ( )

(f) 9 ( )

## QUESTION 13

The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5°. Based on this we must expect a beam of X-rays diffracted at:

(a) 22.0 degrees ( )

(b) 22.5 degrees ( )

(c) 23.0 degrees ( )

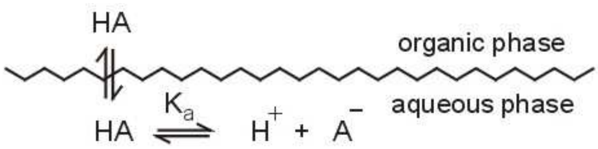
(d) 23.5 degrees ( )

(e) 24.0 degrees ( )

(f) 24.5 degrees ( )

## QUESTION 14

The undissociated form of a weak organic acid HA can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:




Regarding this extraction, are the following statements correct (Y) or not (N)?

(a) The distribution constant ($K_D$) of the acid HA depends on the *pH* of the aqueous phase. (Y) (N)

(b) HA can be efficiently extracted only from acidic aqueous solutions. (Y) (N)

(c) The distribution ratio (D) of the acid HA depends on the pH of the aqueous phase. (Y) (N)

(d) The distribution ratio (D) of the acid HA depends mainly on its concentration. (Y) (N)

## QUESTION 15

Regarding Beer's law, are the following statements correct (Y) or not (N)?

(a) The absorbance is proportional to the concentration of the absorbing compound. (Y) (N)

(b) The absorbance is linearly related to the wavelength of the incident light. (Y) (N)

(c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. (Y) (N)

(d) The transmittance is inversely proportional to the logarithm of absorbance. (Y) (N)

(e) The transmittance is inversely proportional to the concentration of the absorbing compound. (Y) (N)

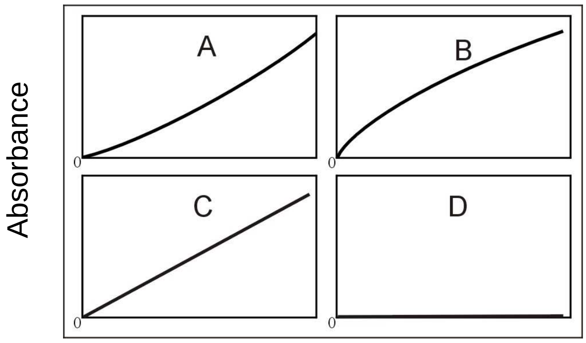
## QUESTION 16

Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics:

| | | |
|---|---|---|
| a) | 3000 Å | 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( ) |
| b) | $5\times10^{14}$ Hz | 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( ) |
| c) | 2000 $cm^{-1}$ | 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( ) |
| d) | $2\times10^{6}$ GHz | 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( ) |

## QUESTION 17

The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:




Total concentration of HX

a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) Pure aqueous solutions of HX were used. Only the anionic species $X^-$ absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

e) Pure aqueous solutions of HX were used. Both HX and $X^-$ absorb. Measurements were obtained at a wavelength where the molar absorptivities of $X^-$ and HX are equal and different than zero. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

## QUESTION 18

Which of the following acids is the strongest?

a) perchloric acid, $HClO_4$ ( )

b) chloric acid, $HClO_3$ ( )

c) chlorous acid, $HClO_2$ ( )

d) hypochlorous, HClO ( )

(e) All of them are equally strong because they all contain chlorine ( )

## QUESTION 19

Which structure describes best the crystal system of iron in which the coordination number is 8?

a) simple cubic ( )

b) body-centered cubic ( )

c) cubic closest packed ( )

d) hexagonal closest packed ( )

e) none of the above ( )

## QUESTION 20

Which of the following elements has the largest third ionization energy?

a) B ( )

b) C ( )

c) N ( )

d) Mg ( )

e) Al ( )

## QUESTION 21

Which second period (row) element has the first six ionization energies (*IE* in electron volts, eV) listed below?

| $IE_1$ | $IE_2$ | $IE_3$ | $IE_4$ | $IE_5$ | $IE_6$ |
|---|---|---|---|---|---|
| 11 | 24 | 48 | 64 | 392 | 490 |

a) B ( )

b) C ( )

c) N ( )

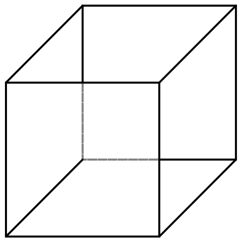
d) O ( )

e) F ( )

# QUESTION 22

Silver metal exists as a face-centered cubic (fcc) packed solid.

a) Draw an fcc unit cell.



b) How many atoms are present in the fcc unit cell?

c) The density of silver has been determined to be 10.5 g cm$^{-3}$ . What is the length of each edge of the unit cell?

d) What is the atomic radius of the silver atoms in the crystal?

# QUESTION 23

Are the following statements correct (Y) or not (N)?

a) HF boils at a higher temperature than HCl. (Y) (N)

b) HBr boils at a lower temperature than HI (Y) (N)

c) Pure HI can be produced by reacting concentrated sulfuric acid with KI. (Y) (N)

d) Ammonia solutions are buffer solutions because they contain the conjugate pair $NH_3$ – $NH_4^+$. (Y) (N)

e) Pure water at 80 °C is acidic. (Y) (N)

f) During electrolysis of an aqueous KI solution with graphite electrodes, the *pH* near the cathode is below 7. (Y) (N)

# QUESTION 24

Under certain conditions of concentration and temperature $HNO_3$ reacts with Zn and its reduction products are $NO_2$ and NO in a molar ratio 1 : 3. How many moles of $HNO_3$ are consumed by 1 mol of Zn?

| | | | | | |
|---|---|---|---|---|---|
| a) | 2.2 | ( ) | d) | 2.8 | ( ) |
| b) | 2.4 | ( ) | e) | 3.0 | ( ) |
| c) | 2.6 | ( ) | f) | 3.2 | ( ) |

# SOLUTIONS FOR SECTION A

**1:** (b); :

**2:** (b);

**3:** (e) is not correct;

**4:** (b);

**5:** (a);

**6:** (c);

**7:** **a)** curve A;

**b)** curve B;

**c)** curve D;

**8:** (b);

**9:** (d);

**10:** **a)** alpha;

**b)** neutron;

**c)** beta;

**d)** gamma;

**e)** gamma;

**11:** (b);

**12:** (c);

**13:** (d);

**14:** **a)** N;

**b)** Y;

**c)** Y;

**d)** N;

**15:** **a)** Y;

**b)** N;

**c)** Y;

**d)** N;

**e)** N;

**16:** **a)** 300 nm;

**b)** 600 nm;

**c)** 5000 nm;

**d)** 150 nm;

**17:** **a)** Curve A;

**b)** Curve B;

**c)** Curve D;

**d)** Curve C;

**e)** Curve C;

**18:** (a);

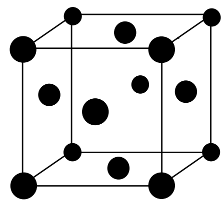
**19:** (b);

**20:** (d);

**21:** (b);

**22:**

**a)**



**b)** 4 atoms,

**c)** The length of each edge of the unit cell is 0.409 nm,

**d)** The atomic radius of the silver atoms in the crystal is 0.145 nm.

**23:** **a)** Y;

**b)** Y;

**c)** N;

**d)** N;

**e)** N;

**f)** N;

**24:** (d)

# SECTION B: PHYSICAL CHEMISTRY

## PROBLEM 25 Muon

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

a) The most common spontaneous disintegration reaction for the muon is:

$\mu \rightarrow e + \bar{\nu}_e + \nu_\mu$,

where $\bar{\nu}_e$ is the electron antineutrino, and $\nu_\mu$ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + \nu_\mu$, carried away a total energy of $2.000\times10^{-12}$ J, while the electron was moving with a kinetic energy of $1.4846\times10^{-11}$ J. Determine the mass of the muon.

b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a $^1H$ nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

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## SOLUTION

a) Energy of a stationary muon:

$E_\mu = m_\mu c^2 = E_e + E_{v,v}$

$m_\mu c^2 = m_e c^2 + (T_e + E_{v,v})$

$$m_\mu = \frac{m_e + (T_e + E_{v,v})}{c^2} = \frac{9.109\times10^{-31} + (1.4846\times10^{-11} + 2.000\times10^{-12})}{(2.998\times10^8)^2} =$$

$= 1.883\times10^{-28}$ kg

b) From Bohr theory:

$$E_n = -\frac{m e^4}{2 n^2 h^2} = -109700 \text{ cm}^{-1} \times \frac{1}{n^2} \times \left(\frac{m}{m_e}\right),$$

where

$$m = \frac{m_{\mu}\, m_{H}}{m_{\mu} + m_{H}}$$

$$\lambda = \frac{1}{E_4 - E_2} = \frac{1}{109700\left(\frac{m}{m_e}\right)\left(\frac{1}{4} - \frac{1}{16}\right)} = 2.615\times10^{-7}\ \text{cm}$$

$$\frac{m}{m_e} = 185.9$$

$$m = 185.9 \times 9.109\times10^{-31} = 1.693\times10^{-28}\ \text{kg}$$

The mass of a proton from Tables attached :

$m_H$ = 1.673×10$^{-27}$ kg

$$m_{\mu} = \frac{m\, m_H}{m_H - m} = \frac{1.693\times10^{-28}\ \times\ 1.673\times10^{-27}}{1.673\times10^{-27} - 1.693\times10^{-28}} = 1.884\times10^{-28}\ \text{kg}$$

## PROBLEM 26 Spectrum of CO

Rotational energy levels of diatomic molecules are well described by the formula $E_J = B$ J(J+1), where J is the rotational quantum number of the molecule and $B$ its rotational constant. Constant $B$ is related to the reduced mass $\mu$ and the bond length $R$ of the molecule through the equation

$$B = \frac{h^2}{8\pi^2 \mu R^2}\ .$$

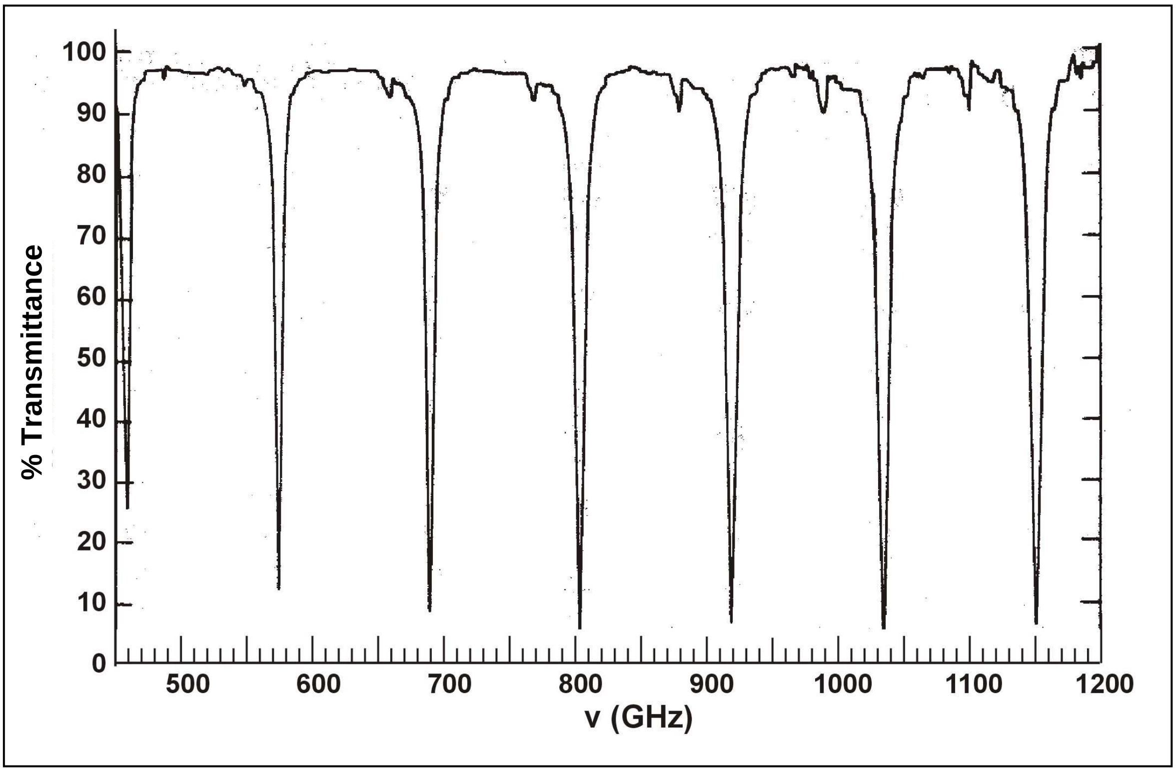
In general, spectroscopic transitions appear at photon energies which are equal to the energy difference between appropriate states of a molecule ($h\ \nu = \Delta E$). The observed rotational transitions occur between adjacent rotational levels, hence $\Delta E = E_{J+1} - E_J = 2\ B\ (J+1)$. Consequently, successive rotational transitions that appear on the spectrum (such as the one shown here) follow the equation $h\ (\Delta v) = 2\ B$.

By inspecting the spectrum provided, determine the following quantities for $^{12}C^{16}O$ with appropriate units:

a) $\Delta v$

b) $B$

c) $R$



## SOLUTION

a) For example: $\Delta v$ = 1150 – 1035 = 115 GHz

b) $B = \frac{h\ \Delta \nu}{2} = \frac{6.63 \times 10^{-34} \times 115 \times 10^{9}}{2} = 3.81 \times 10^{-23}$ J

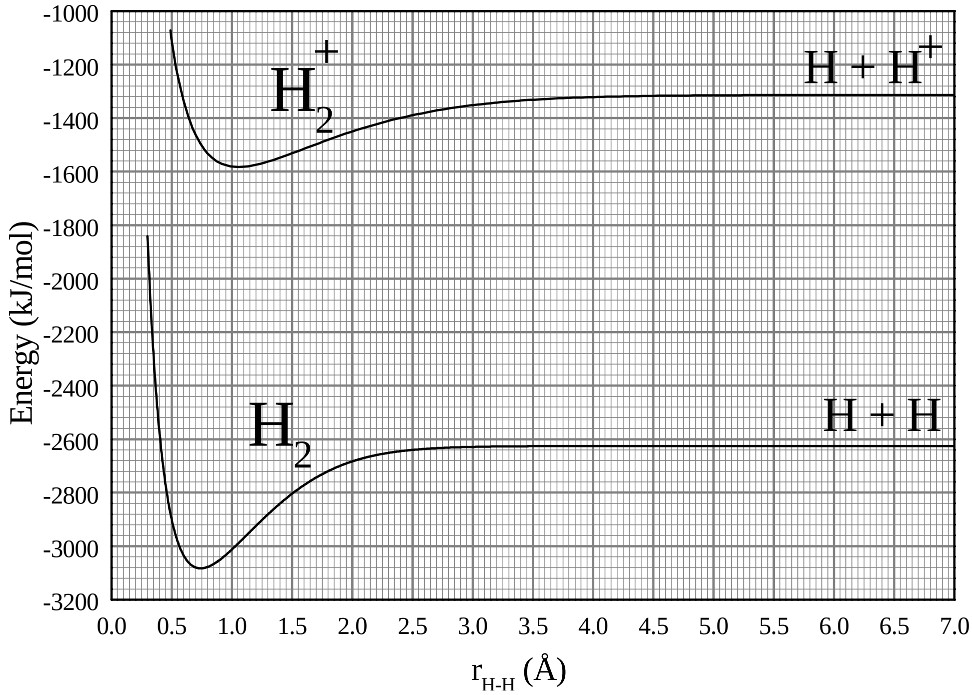
c) $\mu = \frac{m(\text{C}) \times m(\text{O})}{m(\text{CO})} = \frac{12 \times 16}{28} = 6.86 \text{ a.u.} = 1{,}14 \times 10^{-26}$ kg

For interatomic distance $R$:

$$R = \frac{h}{2\pi \sqrt{2\mu B}} = \frac{6.63 \times 10^{-34}}{2 \times 3.14 \sqrt{2 \times 1.14 \times 10^{-26} \times 3.81 \times 10^{-23}}} = 1.13 \times 10^{-10} \text{ m} = 1.13 \text{ Å}$$

# PROBLEM 27 Hydrogen molecule

Using the information provided on this graph, give numerical answers with appropriate units to the following questions:




1. What are the equilibrium bond lengths of $H_2$ and $H_2^+$?
2. What are the binding energies of $H_2$ and $H_2^+$?
3. What is the ionisation energy of the $H_2$ molecule?
4. What is the ionisation energy of the H atom?
5. If we use electromagnetic radiation of frequency $3.9\times10^{15}$ Hz in order to ionise $H_2$, what will be the velocity of the extracted electrons? (Ignore molecular vibrational energy.)

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## SOLUTION

**1.** The equilibrium bond lengths of $H_2$ and $H_2^+$ can be read from the minimum of the curves: $r(H_2)$ = 0.75 Å; $r(H_2^+)$ = 1.05 Å

**2.** The binding energies of $H_2$ and $H_2^+$ can be calculated as the differences in the values for infinitive bond lengths and those for minima of the particular curves:

$E_{bond}(H_2)$ = – 2620 – (– 3080) = 460 kJ mol$^{-1}$

$E_{bond}(H_2^+)$ = – 1310 – (– 1580) = 270 kJ mol$^{-1}$

3. The ionization energy $E_{ion}(H_2)$:

$E_{ion}(H_2)$ = – 1580 – (– 3080) = 1500 kJ mol$^{-1}$

4. $E_{ion}(H)$ = – 1310 – (– 2620) = 1310 kJ mol$^{-1}$

5. $H_2 + h\nu \rightarrow H_2^+ + e^-$

$$E(H_2) + h\nu \rightarrow E(H_2^+) + \frac{m_e v_e^2}{2}$$

$$v_e = \sqrt{\frac{2\,(E(H_2) - E(H_2^+) + h\nu}{m_e}} =$$

$$= \sqrt{\frac{2\left(\dfrac{-3080\times10^3 - (-1510\times10^3)}{6.02\times10^{23}}\right) + 6.63\times10^{-34} \times 4.1\times10^{15}}{9.11\times10^{-31}}} = 492\times10^3\ \text{m s}^{-1}$$

## PROBLEM 28 Cryoscopy

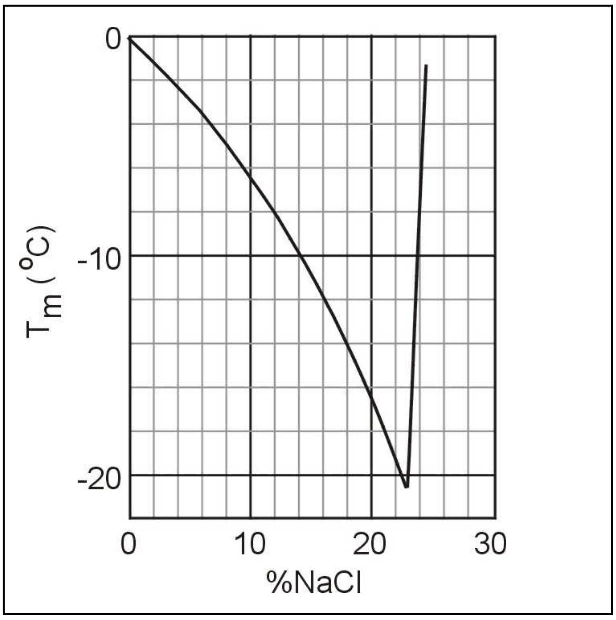
Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point (0 °C) and well above the $CO_2$ sublimation point (–78 °C) this case they mix water ice prepared at its melting point and NaCl. Depending on the quantities used temperatures as low as –20 °C can be reached.

We prepare a cold bath mixing 1 kg of ice at 0 °C with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

a) The mixing process is spontaneous. (Y) (N)

b) The change of entropy during the mixing process is negative. (Y) (N)

c) The following diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is is the freezing point of the bath based on the diagram?




d) If an equal mass of $MgCl_2$ were used instead of NaCl, would the freezing point be higher? (Y) (N)

## SOLUTION

The correct answers are as follows:

a) Y (Yes)

b) N (No)

c) The freezing point of the bath is –9 °C.

d) Y (Yes)

## PROBLEM 29 Pool

A very large swimming pool filled with water of temperature equal to 20 $^{o}$C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine:

a) The heat delivered to the water.

b) Is the change of entropy of the resistor positive, negative, or zero?

(i) $\Delta S_{res} > 0$ ( )

(ii) $\Delta S_{res} = 0$ ( )

(iii) $\Delta S_{res} < 0$ ( )

c) Is the change of entropy of the water positive, negative, or zero?

i) $\Delta S_{pool} > 0$ ( )

(ii) $\Delta S_{pool} = 0$ ( )

(iii) $\Delta S_{pool} < 0$ ( )

d) Is the change of entropy of the system positive, negative, or zero?

(i) $\Delta S_{total} > 0$ ( )

(ii) $\Delta S_{total} = 0$ ( )

(iii) $\Delta S_{total} < 0$ ( )

e) Is the process reversible? (Y) (N)

## SOLUTION

a) $Q = 500\ \text{W} \times 20\ \text{min} \times 60 = 600\ \text{kJ}$

b) $\Delta S_{res} = 0$

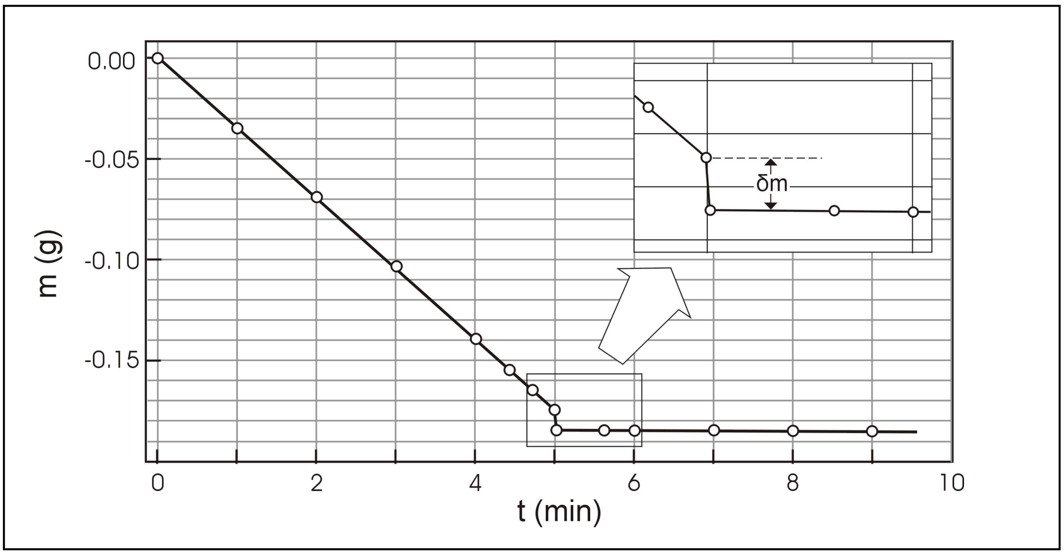
c) $\Delta S_{pool} > 0$

d) $\Delta S_{total} > 0$

e) The answer is No (N).

## PROBLEM 30 Gas velocity

The experiment described here gives a simple way to determine the mean velocity *u* of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time *t* = 0. Balance readings are recorded as shown on the diagram.




At *t* = 5 min the lid is placed over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δ*m*. Therefore, the force exerted on the lid is *f* = δ*m g*. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., *f* = ½ *u* dm/dt. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume *g* = 9.8 m s$^{-2}$.

## SOLUTION

$$\frac{dm}{dt} = \frac{\Delta m}{\Delta t} = \frac{0.14\ \text{g}}{4\ \text{min}} = 0.035\ \text{g min}^{-1} = 5.8\times10^{-4}\ \text{g s}^{-1}$$

$$\delta m\ g = \frac{1}{2} u \frac{dm}{dt}$$

$$u = \frac{0.01\times 9.81\times 2}{5.8\times10^{-4}} = 338\ \text{m s}^{-1}$$

# SECTION C: Organic Chemistry

## PROBLEM 31 Ester identification

2.81 g of an optically active diester **A**, containing only C, H and O were saponified with 30.00 $cm^3$ of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 $cm^3$ of a 1.00 M HCl solution to titrate the unused NaOH only. The saponification products were an optically inactive dicarboxylic acid **B**, MeOH and an optically active alcohol **C**. Alcohol **C** reacted with $I_2$/NaOH to give a yellow precipitate and $C_6H_5COONa$. The diacid **B** reacted with $Br_2$ in $CCl_4$ to give a single, optically inactive product (compound **D**). Ozonolysis of **B** gave only one product.

a) Determine the molecular mass of compound **A**.

b) Give the structural formulas of **A**, **B**, and **C** without stereochemical information.

c) Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.

d) Give the stereochemical formula for **D**, using a Fischer projection.

e) Give the stereochemical formula for **B**.

The diester **A** also reacted with $Br_2$ in $CCl_4$ and was converted to a mixture of two compounds (**E**, **F**) both optically active.

f) Give all the possible stereochemical formulas for **E** and **F**, using Fischer projections. Name all the stereogenic centers as either *R* or *S* on all the formulas.

If we use $Na^{18}OH$ for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

g) Mark the correct answer:

i) Only **B** ( )

ii) Only **C** ( )

iii) Both **B** and **C** ( )

---

## SOLUTION

a) For reaction with diester A 30 – 6 = 24 $cm^3$ of 1.00 M NaOH (0.024 mol NaOH)

Reaction:

ROOC – X – COOR + 2 NaOH $\rightarrow$ NaOOC – X – COONa + 2 ROH

The amount of diester: 0.024 mol / 2 = 0.012 mol

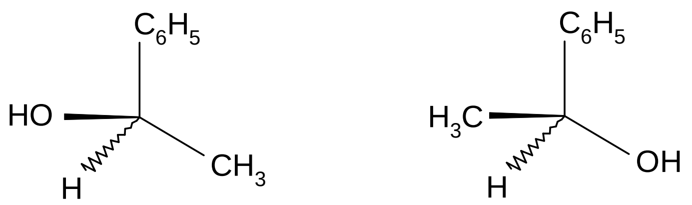
M(A) = 2.81 g / 0.012 mol = 234 g $mol^{-1}$

b) **A**: $H_3COCO-CH=CH-COO(CH_3)C_6H_5$

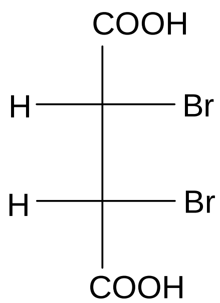
**B**: HOOC-CH=CH-COOH

**C**: $C_6H_5CH(OH)CH_3$

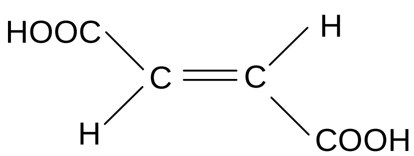
c) Possible stereochemical formulas for **C**:



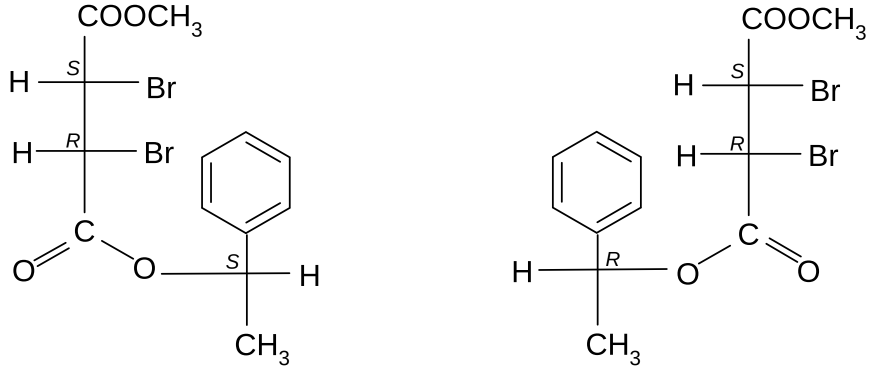

d) Stereochemical formula for **D**:



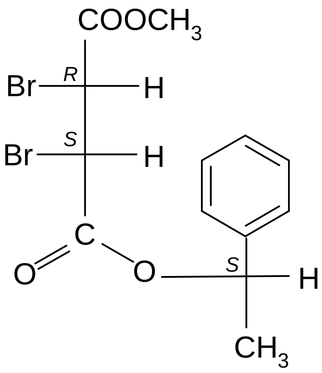

e) Stereochemical formula for **B**:

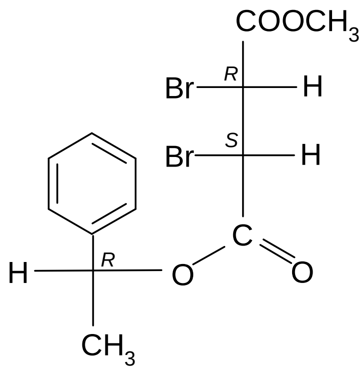



f) Possible stereochemical formula(s) for **E**:



Possible stereochemical formula(s) for **F**:

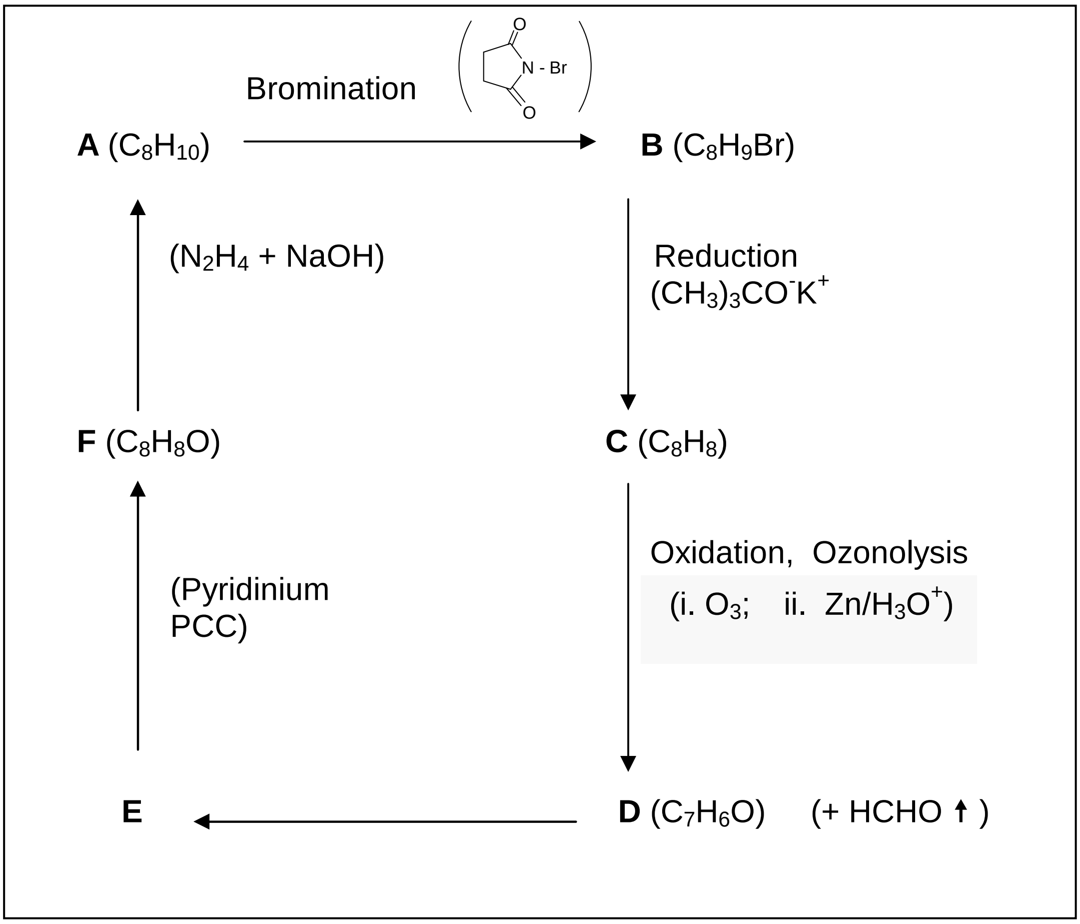


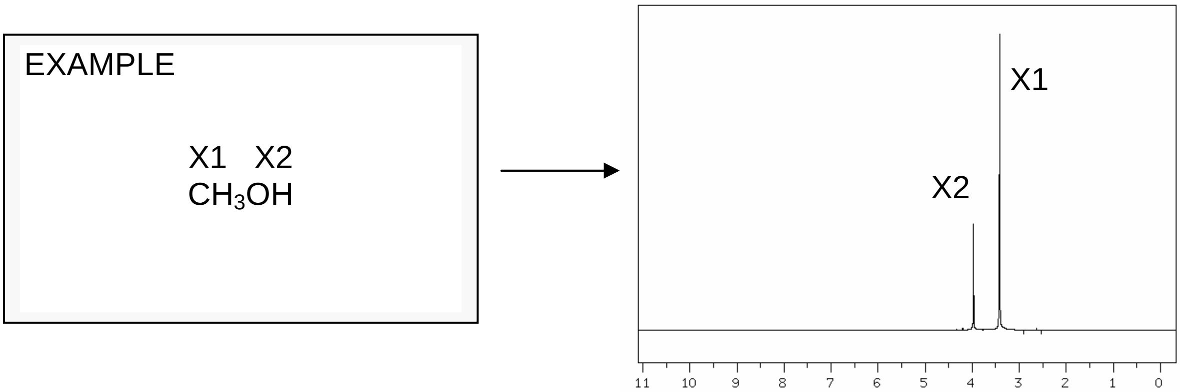

g) Correct answer is ii).

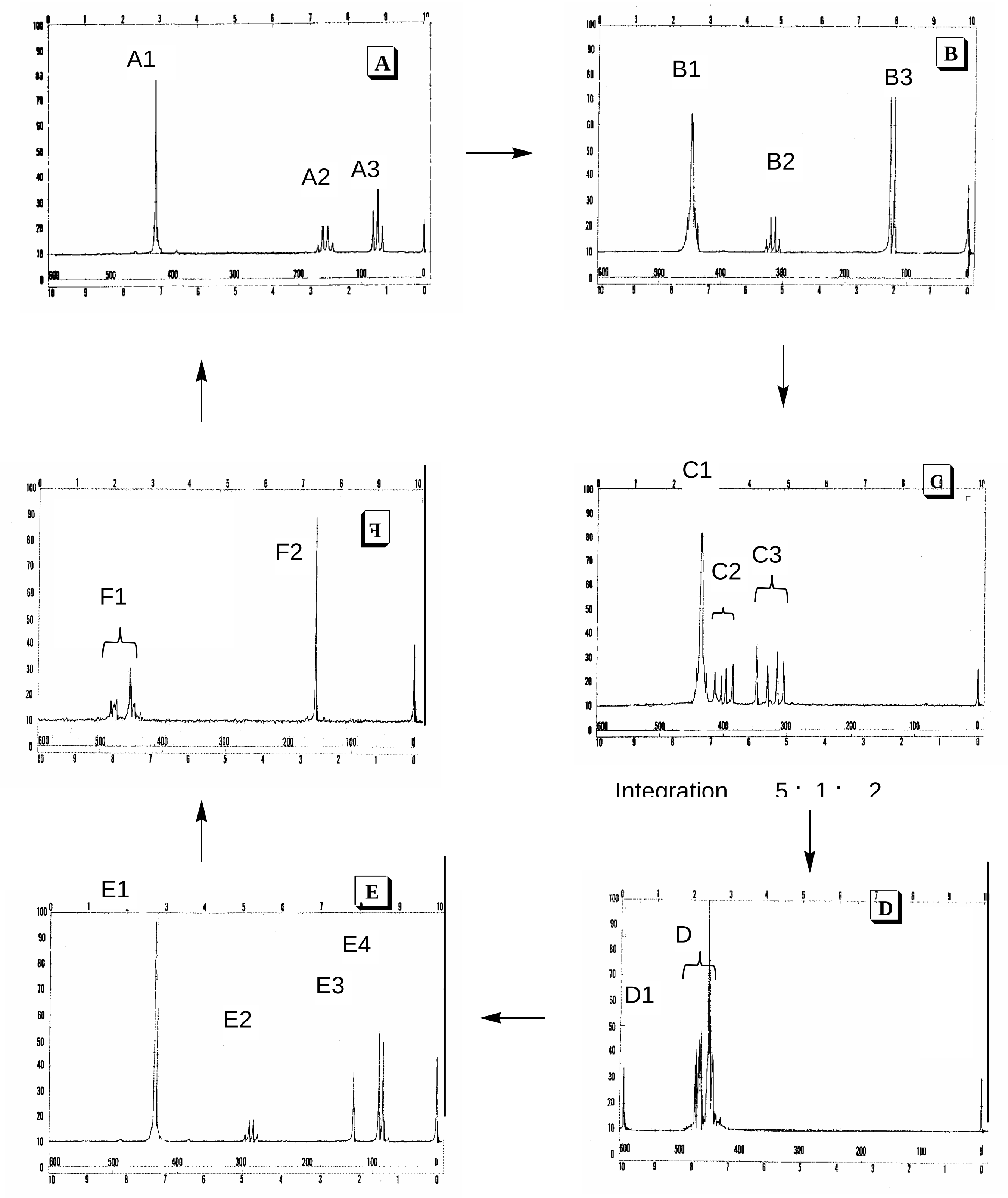
## PROBLEM 32 NMR puzzle

An organic compound **A** ($C_8H_{10}$) gives the following chain of reactions:



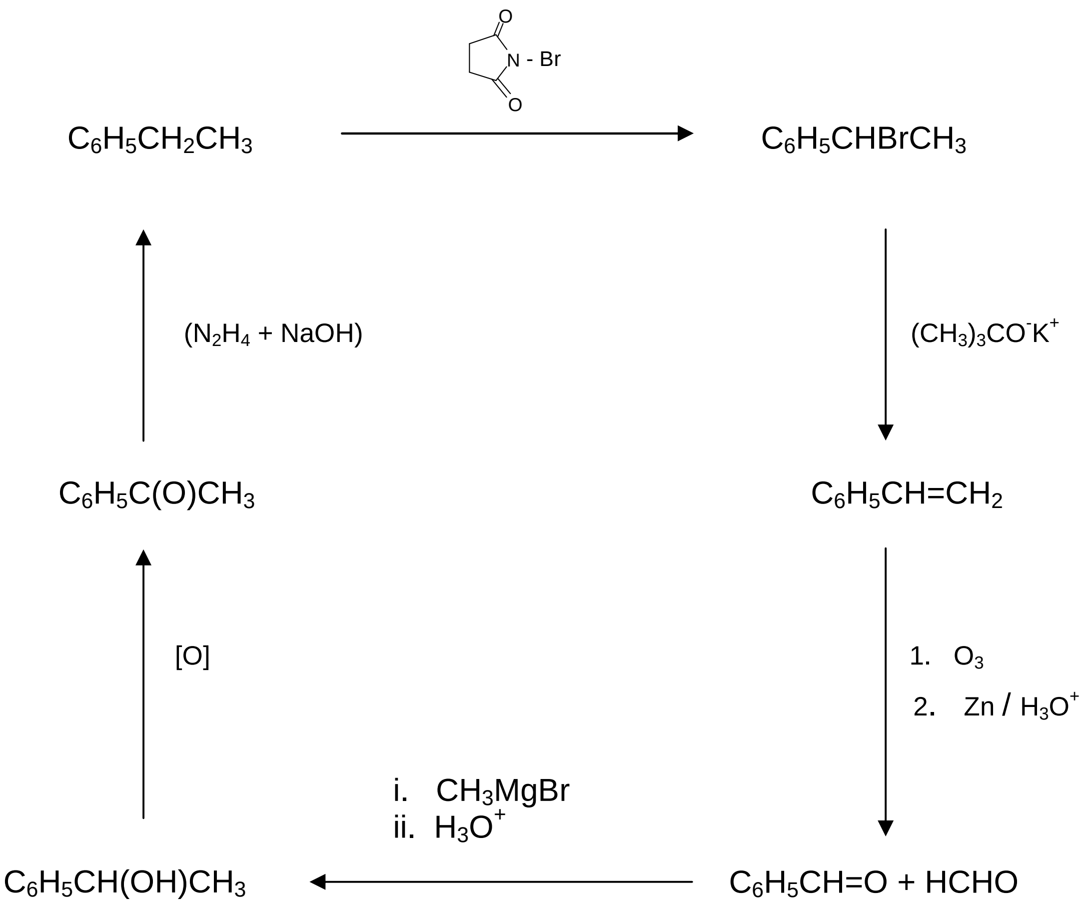

Based on the $^1$H-NMR spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding $^1$H-NMR peaks, as shown in the example.

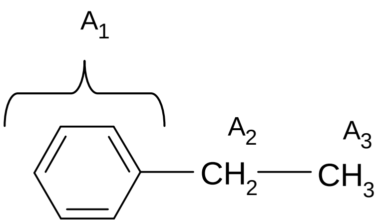




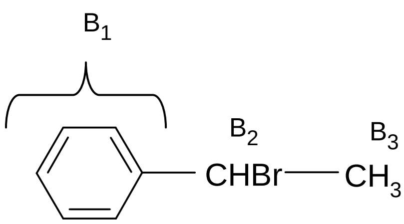

**General remarks:** NMR spectra were ecorded in $CDCl_3$ on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in $CDCl_3$ solutions and catalyse rapid exchange of some particular protons.

## SOLUTION

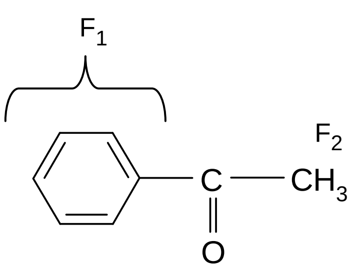


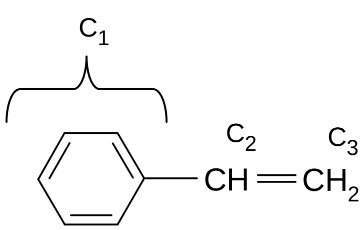

**A**



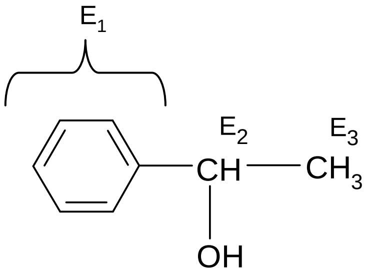

**B**



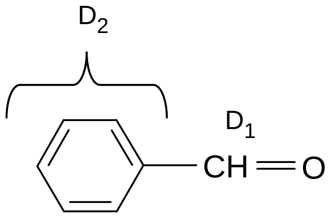

**F**




**C**



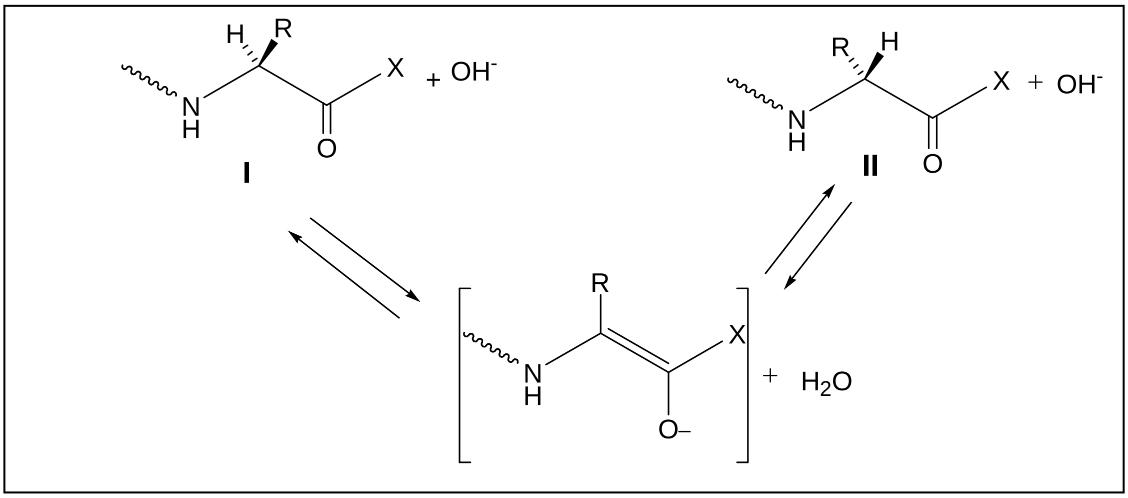

**E**




**D**

# PROBLEM 33 **Peptides**

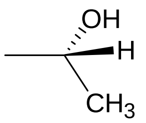
Racemization of α-aminoacids and peptides can occur by an α-enolization mechanism and both heat and the presence of strong bases greatly accelerate the process:




intermediate

**1.** Draw stereochemical formulas **I** and **II** (with bold and dashed bonds) for the aminoacid components of the mixture that has reached equilibrium through the α-enolization mechanism described above operating on each of the following hydroxyaminoacids **A** and **B**:

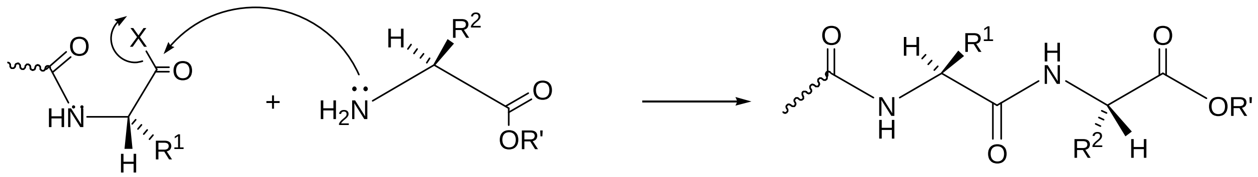
**A**: serine (R = $–CH_2OH$)

**B**: (2*S*,3*R*)-threonine (R =  )

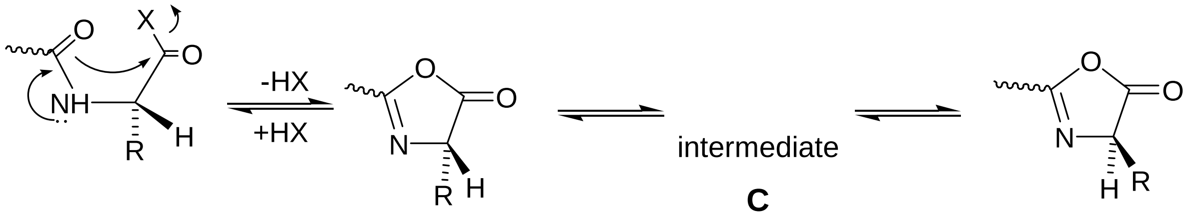

**2.** Mark the box that corresponds to the correct definition of the relationship between the structures you have drawn in each of the above cases A and B.

| | enantiomers | diastereomers |
|---|---|---|
| **A** $_{I, II}$ | ☐ | ☐ |
| **B** $_{I, II}$ | ☐ | ☐ |

During peptide synthesis, in order to form a new peptide bond the carboxyl group has to be activated, that is, it must bear a good leaving group, represented in a simplified scheme below:




It is at this stage of the synthesis that a second racemization mechanism may occur; the amidic carbonyl oxygen is five atoms away from the activated carboxyl group and can intramolecularly attack the activated carboxyl forming a five membered cyclic intermediate (an azalactone) which quickly equilibrates its hydrogen at the stereogenic center, represented in a simplified scheme below:




**3.** Write the structural formula for the intermediate **C** that interconverts the two azalactones and thus explains the scrambling of the stereochemistry at the stereogenic center.

Azalactones are very reactive substances that can still react with the amino group of an aminoacid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

**4.** If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to 40 °C with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$ (**P$_1$**).

a) Propose a structure for substance **P$_1$**.

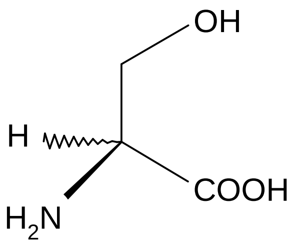
b) Write the reaction product(s) of the substance **P$_1$** with *S*-alanine ethyl ester (**P$_2$**) (the side chain R of the aminoacid alanine is a methyl group) using stereochemical formulas (with bold and dashed bonds) for both reactants and product.

---

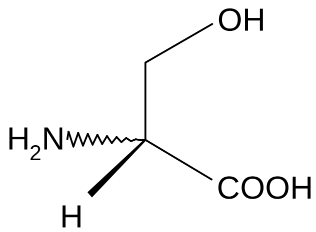
## SOLUTION

**1.**

**A:**

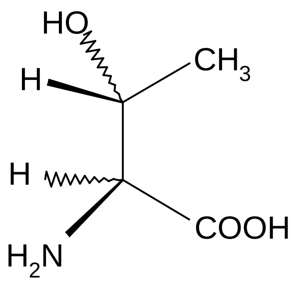


**I**

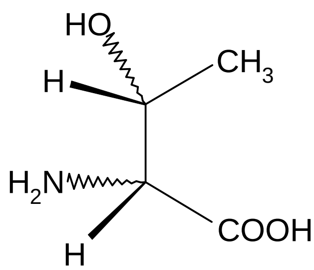


**II**

**B:**



**I**

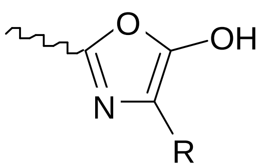


**II**

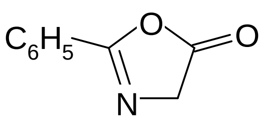
**2.** **A(I)** and **A(II)** are enantiomers**.**

**B(I)** and **B(II)** are diastereomers**.**

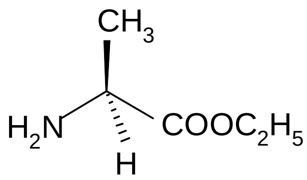
**3.** Intermediate **C**



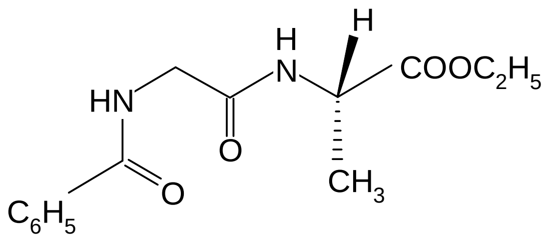
**4.**




Substance **P$_1$**




Ester **P$_2$**




Product

# SECTION D: Inorganic Chemistry

## PROBLEM 34 Aluminium

One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina ($Al_2O_3$) and aluminium metal using the mineral bauxite mined from the Parnassus mountain. Bauxite is a mixed aluminium oxide hydroxide – $AlO_x(OH)_{3-2x}$ where 0<x<1.

Production of Al metal follows a two-stage process:

(i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are $Al_2O_3$ 40 – 60 %, $H_2O$ 12 – 30 %, $SiO_2$ free and combined 1 – 15 %, $Fe_2O_3$ 7 – 30 %, $TiO_2$ 3 – 4 %, F, $P_2O_5$, $V_2O_5$, etc., 0.05 – 0.2 %). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200 °C. Complete and balance the following chemical reactions:

$Al_2O_3 + OH^- + \qquad \rightarrow \quad [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + OH^- \quad \rightarrow \quad SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + \qquad \rightarrow \quad CaSiO_3\downarrow +$

$[Al(OH)_4(H_2O)_2]^- \rightarrow \qquad \downarrow + OH^- + H_2O$

$Al(OH)_3 \rightarrow Al_2O_3 +$

ii) Héroult-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, $Na_3AlF_6$. Typical electrolyte composition ranges are $Na_3AlF_6$ (80 – 85 %), $CaF_2$ (5 – 7 %), $AlF_3$ (5 – 7 %), $Al_2O_3$ (2 – 8 % intermittently recharged). Electrolysis is carried out at 940°C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:

$Al_2O_3(l) + C(anode) \rightarrow Al(l) + CO_2(g)$

Since cryolite is a rather rare mineral, it is prepared according to the following reaction.

Complete and balance this reaction:

$HF + Al(OH)_3 + NaOH \rightarrow Na_3AlF_6 +$

During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

iii) By using the thermodynamic data given below, which are taken to be independent on temperature, determine the thermodynamic quantities Δ*H*, Δ*S* and Δ*G* at 940 °C for the reaction:

C(graphite) + $CO_2$(g) → 2 CO(g).

| | Al(s) | $Al_2O_3$(s) | C (graphite) | CO(g) | $CO_2$(g) | $O_2$(g) |
|---|---|---|---|---|---|---|
| $\Delta_f H^o$ (kJ mol$^{-1}$) | 0 | –1676 | 0 | –111 | –394 | |
| $S^o$ (J.K$^{-1}$ mol$^{-1}$) | 28 | 51 | 6 | 198 | 214 | 205 |
| $\Delta_{fus}H$ (kJ mol$^{-1}$) | 11 | 109 | | | | |

iv) At the same temperature and using the data from the table in part (iii) determine the quantities Δ*H* and Δ*G* for the reaction

2 Al(l) + 3 $CO_2$(g) → $Al_2O_3$(l) + 3 CO(g)

given that Δ*S* = –126 J K$^{-1}$ mol$^{-1}$. (Show your calculations)

v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[Al(H_2O)_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[Al(OH)_4]^-$(aq). In both cases liberation of $H_2$ occurs. $AlF_3$ is made by treating $Al_2O_3$ with HF gas at 700 °C, while the other trihalides, $AlX_3$, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.

vi) The $AlCl_3$ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4 °C) the structure changes to a 4-coordinate molecular dimer, $Al_2Cl_6$. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar $AlCl_3$ molecules.

For the molecular dimer $Al_2Cl_6$, in the gas phase, two different Al–Cl distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding Al–Cl distances.

vii) What is the hybridization of the Al atom(s) in $Al_2Cl_6$ and $AlCl_3$?

## SOLUTION

i) $Al_2O_3 + 2\ OH^- + 7\ H_2O \rightarrow 2\ [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + 2\ OH^- \rightarrow SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + Ca^{2+} \rightarrow CaSiO_3\downarrow + H_2O$

$[Al(OH)_4(H_2O)_2]^- \rightarrow Al(OH)_3\downarrow + 2\ OH^- + 2\ H_2O$

$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$

ii) $2\ Al_2O_3(l) + 3\ C(anode) \rightarrow 4\ Al(l) + 3\ CO_2(g)$

$6\ HF + Al(OH)_3 + 3\ NaOH \rightarrow Na_3AlF_6 + 6\ H_2O$

iii) $$\Delta_r H^0_{1213} = 2\Delta_f H^0_{1213}(CO) - \Delta_f H^0_{1213}(CO_2) = 2 \times (-111) - (-394) = 172\ \text{kJ}$$

$$\Delta_r S^0_{1213} = 2S^0_{1213}(CO) - S^0_{1213}(CO_2) - S^0_{1213}(C) = 2 \times (-198) - 214 - 6 = 176\ \text{J K}^{-1}$$

$$\Delta_r G^0_{1213} = \Delta_r H^0_{1213} - T\Delta S^0_{1213} = 172 - 1213 \times 0.176 = -\ 41.5\ \text{kJ K}^{-1}$$

iv)

$$\Delta_r H^0_{1213} = 3\Delta_f H^0_{1213}(CO) + \Delta_f H^0_{298}(Al_2O_3) + \Delta_{melt} H(Al_2O_3) - 3\Delta_f H^0_{1213}(CO_2) - 2\Delta H_{melt} H(Al) =$$
$$= 3 \times (-111) - (-1676) + 109 - 3 \times (-394) - 2 \times 11 = -740\ \text{kJ}$$

$$\Delta_r H^0_{1213} = 3\Delta_f H^0_{1213}(CO) + \Delta_f H^0_{298}(Al_2O_3) + \Delta_{melt} H(Al_2O_3) - 3\Delta_f H^0_{1213}(CO_2) - 2\Delta H_{melt} H(Al) =$$
$$= 3 \times (-111) - (-1676) + 109 - 3 \times (-394) - 2 \times 11 = -740\ \text{kJ}$$

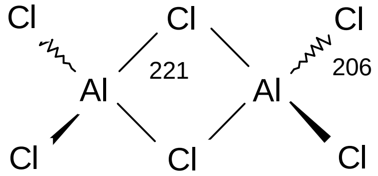
v) $2\ Al + 6\ H^+ + 12\ H_2O \rightarrow 2\ [Al(H_2O)_6]^{3+} + 3\ H_2$

$2\ Al + 2\ OH^- + 6\ H_2O \rightarrow 2[Al(OH)_4]^- + 3\ H_2$

$Al_2O_3 + HF \rightarrow 2\ AlF_3 + 3\ H_2O$

$2\ Al + 3\ X_2 \rightarrow 2\ AlX_3$

vi)




vii) $Al_2Cl_6$ - *sp*$^3$ hybridization

$AlCl_3$ - *sp*$^2$ hybridization

## PROBLEM 35 Kinetics

The acid-catalyzed reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ was found to be of first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by 0.010 mol dm$^{-3}$ was measured under various concentrations of the reactants.

Based on the information provided in the table, answer fulfil the following tasks:

| $[CH_3COCH_3]$ | $[I_2]$ | Time |
|---|---|---|
| (mol dm$^{-3}$) | (mol dm$^{-3}$) | (min) |
| 0.25 | 0.050 | 7.2 |
| 0.50 | 0.050 | 3.6 |
| 1.00 | 0.050 | 1.8 |
| 0.50 | 0.100 | 3.6 |
| 0.25 | 0.100 | … |
| 1.50 | … | … |
| … | … | 0.36 |

a) Derive the rate law for the reaction and calculate the rate constant.

b) Calculate the time needed for 75 % of $CH_3COCH_3$ to react in excess $I_2$.

c) Show graphically the dependence of the rate on $[CH_3COCH_3]$ and on $[I_2]$, for fixed initial concentration of the other reagents.

d) If the rate is doubled by raising the temperature by 10 °C from 298 K, calculate the activation energy for this reaction.

---

## SOLUTION

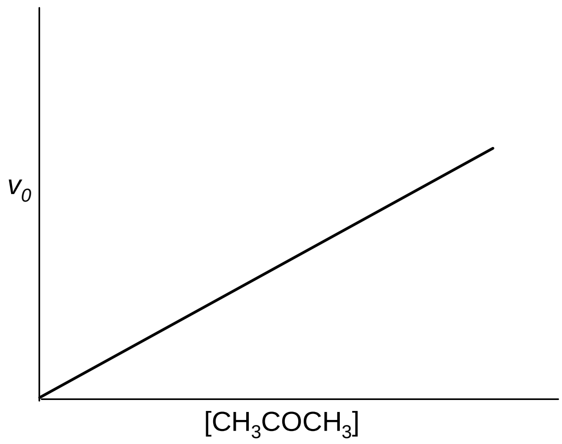
a) $v = k\,[CH_3COCH_3]$

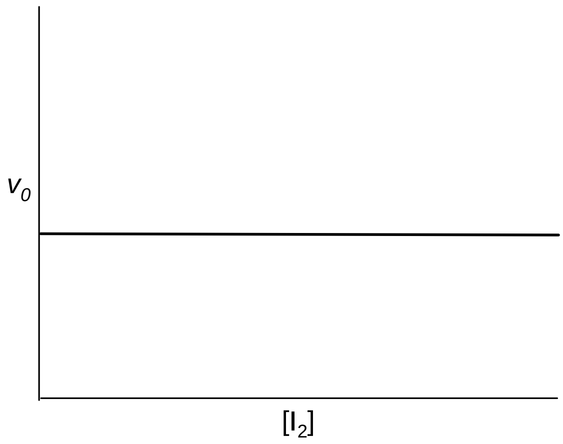
$$k = \frac{v}{[CH_3COCH_3]} = \frac{\frac{0.010}{7.2}}{0.25} = 5.56\times10^{-3}\ \text{min}^{-1} = 9.26\times10^{-5}\ \text{s}^{-1}$$

b) $\tau = \ln 2 / k = 125$ min

$t = 2\ \tau = 250$ min

c)




d)

$$k = A\ \exp\left(-\frac{E_A}{RT}\right)$$

$$\frac{v_2}{v_1} = \frac{k_2}{k_1} = \frac{\exp\left(-\frac{E_A}{RT_2}\right)}{\exp\left(-\frac{E_A}{RT_1}\right)} = \exp\left(-\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\ln\frac{v_2}{v_1} = -\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_A = -R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} \ln\frac{v_2}{v_1}$$

$$E_A = -8.314\left(\frac{1}{308} - \frac{1}{298}\right)^{-1} \ln\frac{2}{1} = 52.9\ \text{kJ mol}^{-1}$$

# PRACTICAL PROBLEMS

## PROBLEM 1 (Practical)

**Synthesis of the Dipeptide *N*-acetyl-*L*-prolinyl-*L*-phenylalanine Methyl Ester (Ac-*L*-Pro-*L*-Phe-OCH$_3$)**

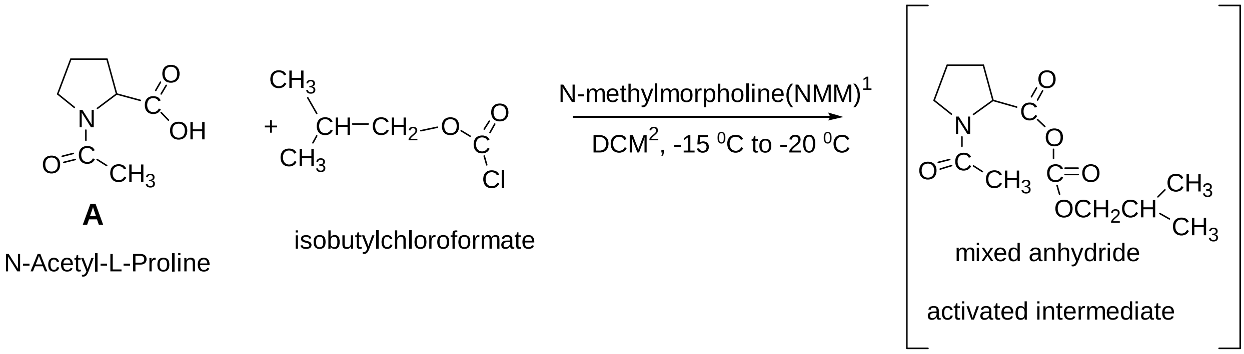
### Introduction

Peptide synthesis is now a well-refined art and many of their synthetic procedures can be readily adapted to the elementary laboratory. Interest in peptides, always high, has heightened even more with the recent discovery of the importance of the so-called "opiate" peptides as well as of other biological active peptides.

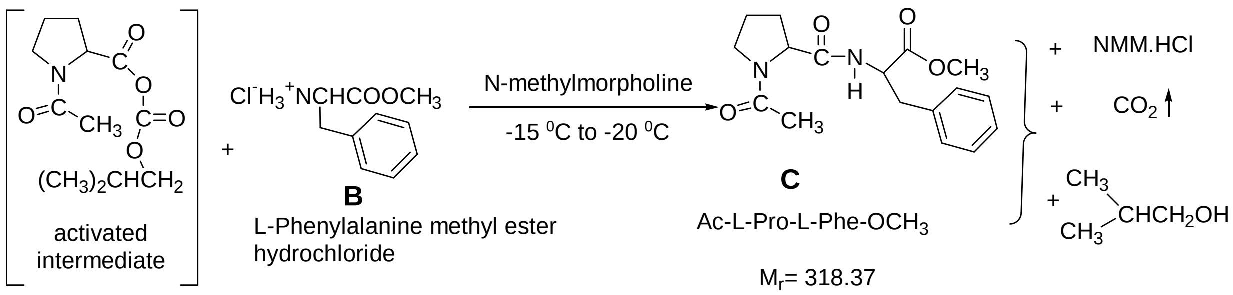
In this experiment the one-pot procedure for synthesizing the title dipeptide from its components, suitably protected amino acids, is described.

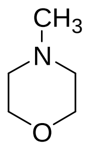
### Reactions

**STEP 1**




**STEP 2**



[1] *N*-methylmorpholine (NMM) = 

[2] DCM = Dichloromethane

**Procedure**

STEP 1

Place the 1.50 g (0.0095 mol) sample of *N*-acetyl-*L*-proline (labelled AcPro), which you have been given, into a 50-$cm^3$ round-bottom flask. Add 20 $cm^3$ dichloromethane (labelled DCM) in the graduated cylinder. Use some of the 20 $cm^3$ DCM to wash out the AcPro vial and add the remaining DCM also into the round-bottomed flask. Plug the flask with a septum, clamp it loosely to a support stand and cool it to –15 °C to –20 °C in the ice/sodium chloride cold bath provided by the supervisor. Allow approximately 5 minutes for cooling. Add 1.2 $cm^3$ (0.0109 mol) of *N*-methylmorpholine (labelled NMM) to the flask, by means of a syringe. Then, slowly add 1.5 $cm^3$ (0.0116 mol) isobutyl-chloroformate (labelled IBCF) to the flask by means of a second syringe. During the addition, swirl the reaction mixture gently by hand, and continue swirling for another 10 min. The temperature should remain in the range –20 °C to –15 °C.

STEP 2

Remove the septum and quickly add all the *L*-phenylalanine methyl ester hydrochloride (2.15 g, 0.0100 mol), (labelled $HCl \cdot H_2NPheOCH_3$) using the polypropylene powder funnel. Plug the flask again with the septum. Immediately add 1.2 $cm^3$ (0.0109 mol) of *N*-methylmorpholine (labelled NMM) using a third syringe, while the reaction mixture is swirled by hand. *ATTENTION: Leave the needle part of the syringe in the septum for the remainder of the reaction*. Allow the reaction to proceed for 60 min at –15 °C to –20 °C, swirling periodically by hand.

*During this waiting period you are highly advised to start working on the Analytical Chemistry experiment.*

After 60 min at –20 °C to –15 °C, remove the 50 $cm^3$ round-bottomed flask from the ice/sodium chloride bath and place the flask in the 250 $cm^3$ beaker and let it warm up to room temperature. Transfer the contents of the flask into the 50 cm$^3$ separating funnel by means of the glass funnel. Rinse the flask with a small amount of dichloromethane (3 – 5 cm$^3$), which is in a vial (labelled DCM). Wash the organic layer successively with two 20 cm$^3$ portions of 0.2 M aqueous HCl solution, two 20 cm$^3$ portions of 1 % aqueous

$NaHCO_3$ solution (read caution comment in next paragraph) and finally one 10 cm$^3$ portion of saturated solution of sodium chloride (labelled brine).

Important

*After each washing allow the separating funnel to stand for enough time, so that the two phases separate completely. Also, take into consideration that the organic phase (DCM) is always the lower layer and contains the product. All the aqueous washings are collected in the same Erlenmeyer flask (empty if necessary).*

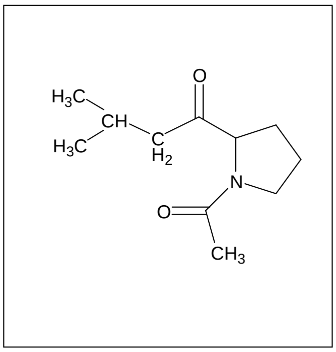
*CAUTION: Keep in mind, also, that during washing with 1 % $NaHCO_3$, the $CO_2$ liberated is exerting pressure on the separating funnel stopper, so be sure to let the gas out through the stopcock before and after each shaking, while holding the funnel upside down.*

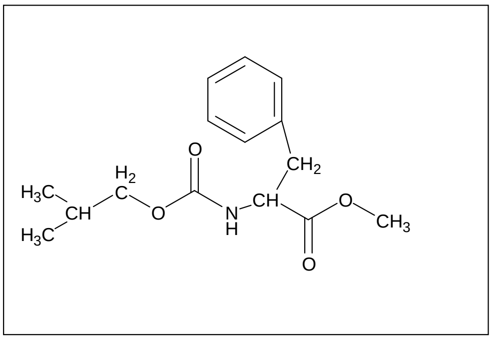
*Before continuing, wash the glass funnel, the 50 cm$^3$ cylinder and the 50 cm$^3$ round-bottom flask with water and then dry them with acetone. Your supervisor will show you where to dispose of the water and the acetone.*

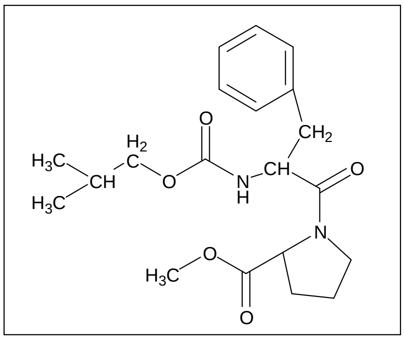
Pour the organic layer into a clean 50 cm$^3$ Erlenmeyer flask. Add the anhydrous sodium sulphate, which is in a vial labelled $Na_2SO_4$, to the Erlenmeyer flask containing the organic layer. The organic phase should become clear. Filter it through the cleaned and dried funnel, whose stem you have previously stuffed with a small piece of cotton to trap any solids, into the cleaned and dried 50 cm$^3$ round-bottom flask. Rinse the Erlenmeyer flask with a small amount of dichloromethane (3 – 5 cm$^3$). Removal of the organic solvent is done under reduced pressure, using a rotary evaporator apparatus. This will be done for you by a laboratory supervisor, who will add 20 cm$^3$ of diethylether to the residue in your flask, which will cause precipitation of your product. After cooling for 5 minutes in the ice bath, scrape the walls of the flask with a spatula, filter by suction the crystallized dipeptide through a fritted glass funnel. Wash twice with diethylether (5 cm$^3$ each time).

Leave the product on the filter under suction for at least 3 minutes. Then collect it on weighing paper, weigh it in the presence of a supervisor and then transfer it into a sample vial and label it with your student code. Write the mass of your product (**C**) on the label and on your answer sheet (on the next page).

During the reaction between the phenylalanine methylester **B** and the activated mixed anhydride intermediate (step 2) the formation of the desired dipeptide product **C** is usually accompanied by a by-product the correct structure of which is one of the three structures **I**, **II**, **III** given below. Circle the Roman numeral corresponding to the correct structure.




**I** **II** **III**

## TLC- Analysis

You have two Eppendorfs, one empty and one with a tiny amount of substance **B**. Put a small amount of **C** into the empty Eppendorf, and dissolve both **B** and **C** in a few drops of methanol. Use the supplied capillary tubes to apply small samples of these solutions to the TLC plate. Develop the TLC plate with a solution of chloroform-methanol-acetic acid (7 : 0.2 : 0.2) as eluant. The appropriate amount of eluant has been placed in the proper vial by the supervisor.

After the elution, analyze the TLC-plate using a UV-lamp. Clearly mark the starting line, solvent front and the UV-active spots.

Draw the diagram in the box on the answer sheet. Determine the $R_f$ values.

Finally place the TLC-plate in a small plastic bag with a sealing strip and put it in an envelope provided by the supervisor. Write your student code on the envelope.

The examination committee will check the quality of the *N*-acetyl-*L*-prolinyl-*L*-phenylalanine methyl ester that you have prepared by determining its angle of optical rotation and consequently its specific rotation, $[a]^t_D$, using an accurate polarimeter apparatus.

# SOLUTION

The following values were required to be written in the Answer Sheet

- Mass of Ac-*L*-Pro-*L*-Phe-$OCH_3$ obtained (product **C**).
- The yield of Ac-*L*-Pro-*L*-Phe-$OCH_3$ **C.**
- The TLC diagram with indication of the base line and the front of the solvent.
- $R_f$ value of *L*-phenylalanine methyl ester hydrochloride (material B) and that of $R_f$ value of Ac-*L*-Pro-*L*-Phe-$OCH_3$ (product C).

- Conclusions from the TLC analysis:
  Compound **C:**
  - Is pure,
  - Contains some **B**,
  - Contains several contaminants,
  - No conclusion.

- Specific rotation of the dipeptide Ac-*L*-Pro-*L*-Phe-$OCH_3$ C (to be measured later by the examination committee)
  $[a]_D^T$ = 45 °

- The correct structure of the by-product: **II.**