Lebanese University
Faculty of Sciences 1

مجلس طلاب الفرع

Entrance exam to faculty of

Medcine

Dentistry

Pharmacy

2011-2012

Chemistry
Mathematics
Physics
English

Chemistry

Concours English. Aziz Kassem

LEBANESE UNIVERSITY
Faculty of Pharmacy

Date: 30/10/2006
Time: 2 hours

Entrance Exam to 2nd
Academic Year 2006-2007

Subject: Chemistry

1- (7 points)
Calculate the enthalpy of the following reaction at 298 K :

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

a. From the bond energies
b. From the standard enthalpies of formation

Given :

Bond	C-H	C=C	C-C	C-O	O-H
Energy ($kJ.mol^{-1}$)	– 357.8	– 423	– 260.4	– 313.5	– 462.3

Compound	$H_2O(g)$	$C_2H_4(g)$	$C_2H_5OH(g)$
ΔH_f^0 ($kJ.mol^{-1}$)	– 241.6	52.5	– 236.2

2- (3 points)
Consider the synthesis reaction of gaseous methanol:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

Given:

	$CO(g)$	$H_2(g)$	$CH_3OH(g)$
ΔH_f^0 at 298 K ($kJ.mol^{-1}$)	– 110.5	0	– 201.2
C_p ($J.mol^{-1}.K^{-1}$)	28.6	27.8	8.4 + 0.25 T

Calculate $\Delta H^0_{reaction}$ at 523 K

3- (6 points)
Consider the following species: B_2 B_2^+ B_2^-

a. Write the electronic configurations of these molecules (Molecular Orbital)
b. Determine the bond orders of each
c. Classify these species in increasing order of bond energies

Given: $_5B$

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4- (6 points)

Consider the following molecules: $SOCl_2$ and SO_3

a. Write the Lewis structure of each molecule

b. Draw and name the geometry of each molecule using VSEPR theory

Given: $_8O$ $_{16}S$ $_{17}Cl$

5- (6 points)

Consider 10 mL of weak diacid H_2A of concentration 10^{-3} mol.L^{-1}

a. Write the reactions of dissociation of H_2A in aqueous solution

b. Calculate the pH of this solution

c. Calculate the pH of the final solution obtained after the addition of the following volumes of base NaOH 10^{-3} mol.L^{-1}

i- 10 mL

ii- 13 mL

Given: $pka_1 = 4$ $pka_2 = 8$

6- (3 points)

Consider the following redox reaction:

$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$$

The equilibrium constant K is equal to 10^8.

Calculate E° of the couple I_3^- / I^- knowing that E° of the couple Fe^{3+} / Fe^{2+} is equal to 0.77 V

7- (6 points)

Consider the following second order reaction:

$$A_2(aq) + B_2(aq) \rightarrow 2AB(aq)$$

At 302 °C, the rate constant k = 2.58×10^{-3} mol^{-1}.L.s^{-1}

$[A_2]_0 = [B_2]_0 = 0.7$ mol.L^{-1}

a. Calculate the time of half reaction $t_{1/2}$

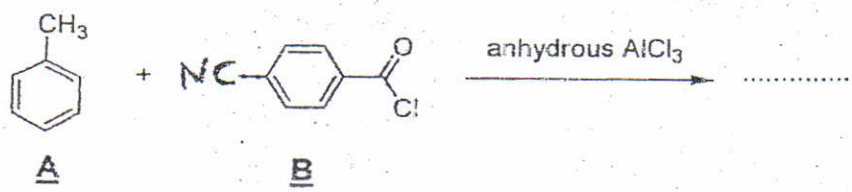
b. Calculate the concentration of AB(aq) after 45 minutes

c. At 508 °C, the rate constant k'= 10^{-2} mol^{-1}.L.s^{-1}. Determine the activation energy E_a

Given : R = 8.3 J.mol^{-1}.K^{-1}

8 – (6 points)

a. Complete the following reaction :



A B

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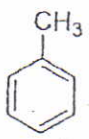
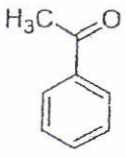
b. What is the type and the name of this reaction.

c. Give the mechanism of this reaction.

d. Compare the reactivity of the following compounds towards the above reaction.



et



A A'

Justify your answer.

9 – (10 points)

When **secondary** alkylbromide **(A)** is treated with a strong base at high temperature, it gives the alkene **(B)**.

(A) **(B)**

a. Complete the representation of **(A)** and give the configuration of the asymetric carbon.

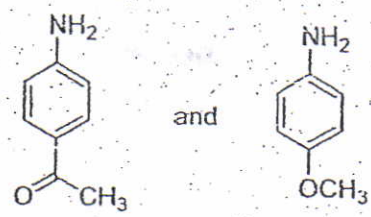
b. Write in details the mechanism of this reaction.

c. The alkene **(B)** is treated with a diluted solution of $KMnO_4$ at low temperature. Give the structure of the obtained product, and precise the optical activity of the reaction medium.

d. The alkene **(B)** is treated with ozone O_3 in presence of H_2O_2/CH_3CO_2H. Write the equation of this reaction.

10 (4 points)

Compare the basicity of the following compounds, justify your answer.

a)  and

b) $H_3C-HC=CH-CH_2^-$ and $H_3C-\overset{O}{\overset{\|}{C}}-CH_2^-$

LEBANESE UNIVERSITY
Faculty of Pharmacy

Duration : 1 hour
Date : October 7th 2008

Entrance exam to 2nd year – Academic year 2008-2009
Subject : Chemistry

Exercise I (10 pts)

Consider the following reaction: $HA + H_2O \rightleftarrows A^- + H_3O^+$

1. Calculate the standard enthalpy and the standard entropy changes of the reaction at 298 *K*
2. Calculate the standard free energy change at 298 *K*. Determine the equilibrium constant K_a at 298 *K*
3. Calculate K_a at 398 *K* assuming that the enthalpy change of this reaction remains constant between 298 and 398 *K*
4. Deduce the effect of temperature on the equilibrium constant, K_a, of HA in aqueous solution

Given at 298 *K*

	HA	A^-
$\Delta H_f°$ ($kJ.mol^{-1}$)	– 651	– 649
$S°$ ($J.mol^{-1}.K^{-1}$)	8	17

$\Delta H_f°$ (H_2O liquid) = $\Delta H_f°(H_3O^+)$
$S°$ (H_2O liquid) = $S°(H_3O^+)$
$R = 8.3\ J.mol^{-1}.K^{-1}$

Exercise II (10 pts)

A- A 1 *L* solution (S_0) contains 0.1 *moi* of a weak diacid H_2A. Calculate the pH of this solution

B- 0.1 *mol* of HA^- were added to the solution (S_0). A new solution (S_1) was obtained.

1. Calculate the pH of the solution (S_1). Give the character of this solution
2. Calculate the pH of the solution obtained when 0.05 *mol* of a strong acid HCl is added to (S_1)

Given for H_2A: $pK_{a1} = 4$ $pK_{a2} = 10$

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Exercise III (10 pts)

The half life of the following first order reaction is $t_{1/2} = 120\ s$ at 20°C

A → 3B + C

1. Calculate the rate constant k
2. Calculate the percent of A remaining after 600 s
3. Determine the activation energy of this reaction knowing that the value of its rate constant doubles when the temperature increases from 20°C to 120°C
4. State the influence of the addition of a catalyst on the activation energy

Given: $R = 8.3\ J.mol^{-1}.K^{-1}$

Exercise IV (7 pts)

Consider the following cell:

(1) $Zn(s) \mid Zn^{2+}(C_1) \parallel Ag^{+}(C_2) \mid Ag(s)$ (2)

Where $C_1 = 0.30\ mol.L^{-1}$ and $C_2 = 0.18\ mol.L^{-1}$.

1. Determine the potential of each electrode. Deduce the polarity of the cell and give the equation of the corresponding reaction
2. Calculate the equilibrium constant K
3. Deduce the composition of the cell when the cell ceases to function

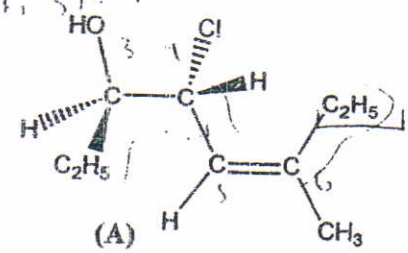
Given: $E°(Zn^{2+}/Zn(s)) = -0.76\ V$; $E°(Ag^{+}/Ag(s)) = +0.80\ V$

Exercise V (3 pts)

1. Write the electronic configuration of the molecular orbitals (**without drawing the MO diagram**) for each of the following species: F_2 ; F_2^{+} ; F_2^{-}
   The atomic number of F is $Z = 9$.
2. Determine the bond order for each species. Compare their bond lengths

Exercise VI (5.5 pts)

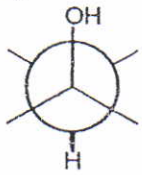
Consider the following compound:



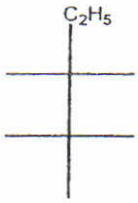
(A)

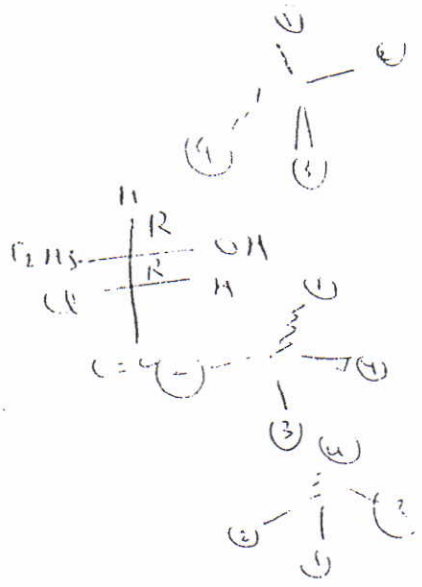
1) Give the systematic name for compound (A) including stereochemistry.

2) Complete the following Newman projection for (A).



3) Complete the following Fisher projection for (A).

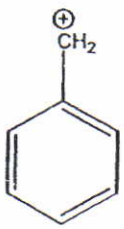




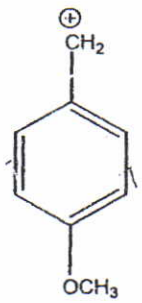
Exercise VII (2 pts)

In each of the following series, indicate (without justification):

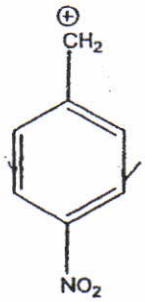
1) The most stable carbocation



a

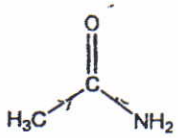


b

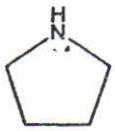


c

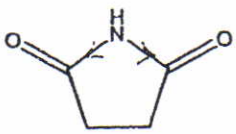
2) The most basic compound



a'



b'



c'

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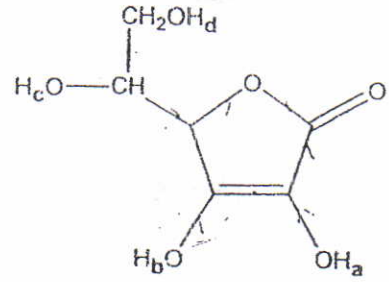
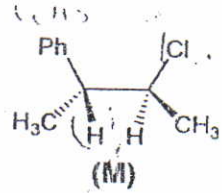
Exercise VIII (1.5 pts)

Choose the most acidic hydrogen (a, b, c or d) in the following compound.



Exercise IX (6.5 pts)

When molecule (M) is treated with CH_3O^-, a mixture of three products A and A' ($C_{10}H_{12}$) and B ($C_{11}H_{16}O$) was obtained.

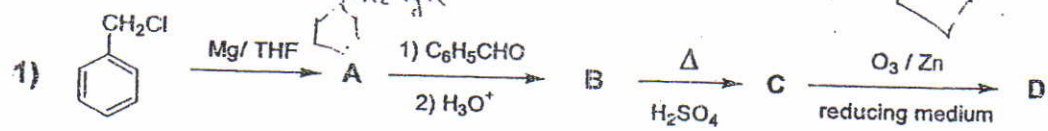


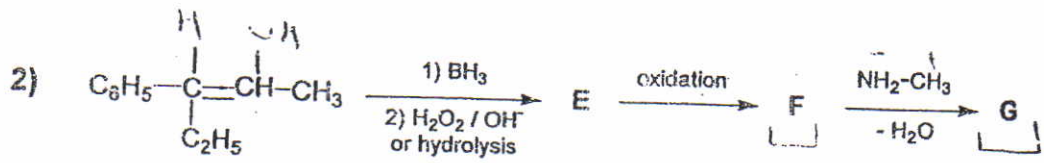
(M)

1) Give the structure of A (major) and A' (minor).
2) Write the detailed mechanism (kinetic order, rate, stereochemistry, ...) leading to compound A.
3) Give the structure of compound B and indicate its stereochemistry (without mechanism). Indicate whether B is optically active or not.

Exercise X (4.5 pts)

Complete the following sequence of reactions (without mechanism)





Good Luck

LEBANESE UNIVERSITY
Faculty of Medical Sciences
Faculty of Dentistry

Time: 1 h
October 12, 2009

Entrance Exam 2009-2010
Subject: Chemistry

Exercise I (8 pts)

Given the following solutions:

Solution A : Chloroacetic acid, $Cl\text{-}CH_2\text{-}COOH$ $0.25\ mol.L^{-1}$

Solution B : NaOH $0.50\ mol.L^{-1}$

a. What is the pH of solution A ($pK_a = 2.85$)?

b. 50 mL of solution A are mixed with 10 mL of solution B. Calculate the pH of the final solution.

Exercise II (11 pts)

Consider at 298 K, the following equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Given : $R = 8.31\ J.mol^{-1}.K^{-1}$

	$O_2(g)$	$SO_2(g)$	$SO_3(g)$
$\Delta H^0_f (KJ.mol^{-1})$	0	-296	-395
$S^0 (J.mol^{-1}.K^{-1})$	205	248	256
$C_p (J.mol^{-1}.K^{-1})$	$29 + 13.6\times10^{-3}\ T$	$40 + 42.6\times10^{-3}\ T$	$50 + 45.0\times10^{-3}\ T$

a. Calculate the enthalpy ΔH^0_r , the entropy ΔS^0_r and the free energy ΔG^0_r of the reaction.

b. Calculate the equilibrium constant, K_p at 298 K.

c. Determine the enthalpy of the reaction, ΔH^0_r at 798 K

Exercise III (8 pts)

Consider the second order reaction : $H_2 + Cl_2 \longrightarrow 2HCl$

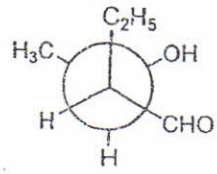
H_2 and Cl_2 are reacted at 27 °C, each with a concentration 0.01 $mol.L^{-1}$. After 2 hours, the measured concentration of H_2 is $5x10^{-3}$ $mol.L^{-1}$.

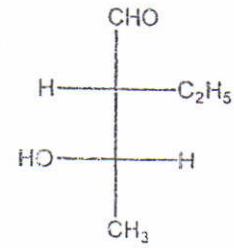
a. What is the value of the time of half reaction, $t_{1/2}$? Calculate the rate constant, k.

b. At 227 °C, the reaction rate is multiplied by 4. Determine the new $t_{1/2}$ of the reaction as well as its activation energy. *Given : $R = 8.31\ J.mol^{-1}.K^{-1}$*

Exercise IV (1 pt)

Indicate, without **justification**, the stereochemical relationship between the given pair.

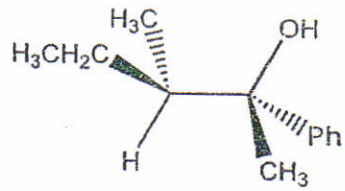




Exercise V (8 pts)

Consider the following compound **A** :

A



1- Give the systematic (IUPAC) name of compound **A**.

2- Compound **A** is treated at room temperature with aqueous HCl.

a- Write the equation for the reaction.

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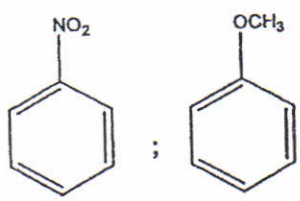
b- Give a detailed mechanism for the formation of the product(s) (reaction rate, intermediate, stereochemistry...).

Exercise VI (2 pts)

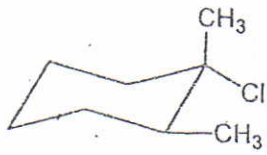
In the given pair of compounds indicate the most reactive and the type of reaction (S_N, elimination, electrophilic addition, nucleophilic addition, electrophilic aromatic substitution....). Briefly explain.



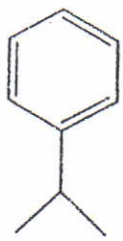
with $Cl_2/AlCl_3$

Exercise VII (2 pts)

Complete the following reactions :

A- 

$EtO^- Na^+, \Delta$ ..... (major)

B-  conc. $KMnO_4$ .....

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LEBANESE UNIVERSITY
Faculty of Pharmacy

Duration: 2 h
September 20, 2010

Entrance Exam 2010-2011
Subject: Chemistry

Exercise I (9 pts)

A thermodynamic study shows that the following reaction has an enthalpy change $\Delta H° = -78$ kJ and an entropy change $\Delta S° = -202\ J.K^{-1}$ at $T = 305$ K

$$A + B_2 \rightleftharpoons AB_2$$

1) Calculate $\Delta G°$ and comment on its sign.

2) Write the relation that allows to calculate $\Delta S°$ knowing that of $\Delta S°_{298}$

3) Calculate the equilibrium constant at 305 K then calculate its value at 298 K assuming that $\Delta H°$ is constant in the given interval of temperature. Compare the values of the equilibrium constants and deduce the direction in which the equilibrium shifts

4) Deduce $\Delta G°$ at 298K

Given: $R = 8.31\ J.mol^{-1}K^{-1}$

Exercise II (9 pts)

One liter of a buffer solution is prepared by mixing 0.01 mol of a weak diacid H_2A and 0.03 mol of its salt NaHA

1. Calculate the pH of the buffer solution

2. Calculate the pH of the solution obtained when 0,005 mol of a strong acid HBr are added to the buffer solution

3. Calculate the pH of the solution obtained when 0.004 mol of a strong base KOH are added to the buffer solution

4. What can you deduce?

Given: Ka (H_2A/HA^-) = 6.2×10^{-8}

Exercise III (9 pts)

The kinetics of the following reaction in aqueous solution is studied:

$$AX \longrightarrow A^+ + X^-$$

The variation of the concentration of AX as a function of time is given in the following table :

Time (s)	0	575	1090	1720
[AX] ($mol.L^{-1}$)	0.1	0.085	0.074	0.063

1. Show that the reaction is first order

2. Calculate the rate constant and the half life time $t_{½}$

3. The activation energy of this reaction is E_a= 125 $kJ.mol^{-1}$ at 25°C. At the same temperature and in the presence of a catalyst it becomes E_a'= 100 $kJ.mol^{-1}$. Calculate the ratio k'/k

Given : R = 8.31 $J.mol^{-1}K^{-1}$

Exercise IV (6 pts)

A- Balance the following reaction in basic medium:

$$ClO^- + CrO_2^- \rightleftharpoons CrO_4^{2-} + Cl^-$$

B- Consider the following two solutions:

Solution (1) : Cr^{3+} (10^{-1} mol.L^{-1}), Cr^{2+} (10^{-3} mol.L^{-1})

Solution (2) : V^{3+} (10^{-3} mol.L^{-1}), V^{2+} (10^{-1} mol.L^{-1})

1. Calculate the electrode potential E of each electrode

2. Write the global reaction of the redox reaction taking place between these two solutions

3. Calculate the potential of the reaction and its equilibrium constant K

Given: $E°\ (Cr^{3+}/Cr^{2})$= - 0.407 V $E°(V^{3+}/V^{2+})$= - 0.255 V

Exercise V (5 pts)

A- The electron of hydrogen atom at the fundamental state is excited by a radiation of wavelength λ= 97.35 nm.

1. To which energy level was the electron excited?

2. Calculate in kJ the energy needed to ionize one mole of hydrogen atom from the ground state

Given: $R_H = 1.091\times10^{7}\ m^{-1}$ $N_A = 6.023\times10^{23}\ mol^{-1}$ $1\ nm = 10^{-9}\ m$
$c = 3\times10^{8}\ m.s^{-1}$ $h = 6.626\times10^{-34}\ J.s$

B- Consider the following species: O_2 O_2^- O_2^{2-}

1. Write the electronic configuration of the molecular orbitals of each species

2. Determine the bond order of the corresponding bonds

3. Classify by increasing order the bond energies of the corresponding bonds

Exercise VI (2 pts)

The dissolution of 20 g of a solid none electrolyte solute A, in 1 Kg of water lowers the vapor pressure of 0.2 mm Hg.

1. Find the molar fraction X_A of A knowing that the vapor pressure of pure water is 32 mm Hg at the same temperature

2. Calculate the molar mass of (A)

Given : $M(H_2O) = 18\ g.mol^{-1}$

3) $\Delta G = \Delta H - T\Delta S = -78 - 305(-202\times10^{-3}) = -16.39\ kj$ (1/2)

$\Delta G^\circ < 0 \Rightarrow$ la réaction est spontanée dans le sens direct (1/2)

2) $\Delta S^\circ_{rT} = \Delta S^\circ_{r\,298} + \int_{298}^{T} \Delta C_p \frac{dT}{T}$ (1)

3) $\Delta G^\circ_r = -RT\ln K \Rightarrow K = e^{-\frac{\Delta G^\circ}{RT}}$ (1) $= e^{\frac{16.39}{8,31\times10^{-3}\times305}} = 643.3$ (1/2)

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ (1)

$$\Rightarrow \ln\frac{K_{298}}{K_{305}} = \frac{-78}{8.31\times10^{-3}}\left(\frac{1}{305} - \frac{1}{298}\right)$$ (1/2)

$$= \frac{-78000}{8,31}\left(\frac{298-305}{305\times298}\right)$$

$$= 0,723$$ (1/2)

$\Rightarrow \ln K_{298} = 7.19$

d'où $K_{298} = e^{7.19} = 1326$ (1/2)

$\Delta H^\circ_r < 0 \Rightarrow$ la diminution de la température déplace l'équil dans le sens exothermique $\Rightarrow$ dans le sens 1 (1)

4) $\Delta G^\circ_{298} = -RT\ln K_{298} = -8.31\times298\times\ln 1326 = -17,804\ kj$ (1/2)

1) Correction exercice ...

1- $H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$ $\quad K_a = 6,2.10^{-8}$

$pK_a = 7,2$

Solution tampon formée par le couple H_2A / HA^-

(1) $pH = pK_a + \log \frac{[HA^-]}{[H_2A]} = pK_a + \log \frac{n_{HA^-}}{n_{H_2A}}$ (1)

$= 7,2 + \log \frac{0,03}{0,01} = \underline{7,68}$

2- $HA^- + H_3O^+ \longrightarrow H_2A + H_2O$ (1)

	HA^-	H_3O^+	H_2A
EI	0,03	0,005	0,01
EF	0,03-0,005	ε	0,01+0,005

(2)

$pH = pK_a + \log \frac{n_{HA^-}}{n_{H_2A}} = 7,2 + \log \frac{0,03-0,005}{0,01+0,005}$

$pH = \underline{7,42}$ (1)

3- $H_2A + HO^- \longrightarrow HA^- + H_2O$

	H_2A	HO^-	HA^-
EI	0,01	0,004	0,03
EF	0,01-0,004	ε	0,03+0,004

ΔpH négligeable (1)

$pH = pK_a + \log \frac{n_{HA^-}}{n_{H_2A}} = 7,2 + \log \frac{0,03+0,004}{0,01-0,004}$

$pH = \underline{7,95}$ (1)

→ Suite

1) Ordre 1 $\Rightarrow \underset{(1)}{\ln \frac{a}{a-x}} = kt \Rightarrow \ln \frac{0,1}{0,085} = K_1 \times 575 \Rightarrow K_1 = 2,8 \times 10^{-4}$

(1) $\ln \frac{0,1}{0,075} = K_2 \times 1090 \Rightarrow K_2 = 2,75 \times 10^{-4}$

$\ln \frac{0,1}{0,063} = K_3 \times 1720 \Rightarrow K_3 = 2,74 \times 1$

$K_1 \simeq K_2 \simeq K_3 \Rightarrow$ l'ordre 1 est vérifié (1)

3

---

2) $K = \frac{K_1 + K_2 + K_3}{3} = 2,76 \times 10^{-4}\ s^{-1}$ (1)

3

ordre 1 $\Rightarrow t_{1/2} = \underset{(1)}{\frac{\ln 2}{K}} = \frac{0,69}{2,76 \times 10^{-4}} = 2500\ s$ (1/2)

---

3) Loi d'Arrhenius $\Rightarrow K = A e^{-\frac{E_a}{RT}}$ (1)

$\Rightarrow \ln K = \ln A - \frac{E_a}{RT}$

et $\ln K' = \ln A - \frac{E_a'}{RT}$

$\Rightarrow \ln \frac{K}{K'} = \frac{1}{RT}(E_a' - E_a)$

$\Rightarrow \ln \frac{K}{K'} = \frac{1}{8,31(27+273)}(106 - 125) \times$ (1)

$\Rightarrow \ln \frac{K}{K'} = -10,03$

$\Rightarrow \frac{K}{K'} = 4,41 \times 10^{-5}$

d'où $\frac{K'}{K} = 22653$ (1)

3

Exercice IV

A]

$3\times\ ClO^- + 2e^- + H_2O = Cl^- + 2HO^-$ (1/2)

$2\times\ CrO_2^- + 4HO^- = CrO_4^{2-} + 3e^- + 2H_2O$ (1/2)

$3ClO^- + 2CrO_2^- + 2HO^- = 3Cl^- + 2CrO_4^{2-} + H_2O$ (1/2) — 1 1/2

3] 1) $Cr^{3+} + e^- = Cr^{2+}$

$E_1 = E^\circ_{1(Cr^{3+}/Cr^{2+})} + \frac{0,059}{n} \log \frac{[Cr^{3+}]}{[Cr^{2+}]}$ (1/2)

$E_1 = -0,407 + \frac{0,059}{1} \log \frac{10^{-1}}{10^{-3}}$ — 1

$E_1 = \underline{-0,289V}$ (1/2)

$V^{3+} + e^- = V^{2+}$

$E_2 = E^\circ_{2(V^{3+}/V^{2+})} + \frac{0,059}{n} \log \frac{[V^{3+}]}{[V^{2+}]}$ (1/2)

$E_2 = -0,255 + 0,059 \log \frac{10^{-3}}{10^{-1}}$

$E_2 = \underline{-0,373V}$ (1/2) — 1

$E_1 > E_2$

2) $Cr^{3+} + V^{2+} \longrightarrow Cr^{2+} + V^{3+}$ (1/2) — 1/2

---

3) $E = E_1 - E_2 = -0,289 - (-0,373)$

$= \underline{0,084\,V}$ (1/2)

$K = 10^{\frac{n(E_1^\circ - E_2^\circ)}{0,059}} = 10^{\frac{1 \times (-0,152)}{0,059}}$ (1)

$= \underline{2,65 \cdot 10^{-3}}$ (1/2) — 2

$n_{e^- global} = 1$

$E_1^\circ - E_2^\circ = -0,407 - (-0,255) = -0,152$

H- $\frac{1}{\lambda} = K_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ (½)

$\Rightarrow \frac{1}{97,53 \times 10^{-9}} = 1,091 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right)$

$\Rightarrow n_2 = 4$ (½)

2- $E = \frac{hc}{\lambda} = hc R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ (½)

- avec $n_1 = 1$ et $n_2 = \infty$

$\Rightarrow E = 6,626 \times 10^{-34} \times 3 \times 10^8 \times 1,091 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty} \right)$

$\Rightarrow E = 21,69 \times 10^{-19}$ J/ atome

$\Rightarrow E = 130,64 \times 10^4$ J/mol soit 1306,4 KJ/mol (½)

3) (½) O_2 : $(6_{1s})^2 (6^*_{1s})^2 (6_{2s})^2 (6^*_{2s})^2 (6_{2p_z})^2 (\Pi_{2p_x})^2 (\Pi_{2p_y})^2 (\Pi^*_{2p_x})^1 (\Pi^*_{2p_y})^1 (6^*_{2p_z})^0$

(½) O_2^- : $(6_{1s})^2 (6^*_{1s})^2 (6_{2s})^2 (6^*_{2s})^2 (6_{2p_z})^2 (\Pi_{2p_x})^2 (\Pi_{2p_y})^2 (\Pi^*_{2p_x})^2 (\Pi^*_{2p_y})^1 (6^*_{2p_z})^0$

(½) O_2^{2-} : $(6_{1s})^2 (6^*_{1s})^2 (6_{2s})^2 (6^*_{2s})^2 (6_{2p_z})^2 (\Pi_{2p_x})^2 (\Pi_{2p_y})^2 (\Pi^*_{2p_x})^2 (\Pi^*_{2p_y})^2 (6^*_{2p_z})^0$

) Indice de liaison : pr $n = \frac{1}{2}$ (nē liants − nē antiliants).

$n_{O_2} = 2$ $n_{O_2^-} = 3/2$ $n_{O_2^{2-}} = 1$ (1 pt tout)

) $E_{O_2^{2-}} < E_{O_2^-} < E_{O_2}$ (½)

Exercice VI — Propriétés colligatives

1/ $\Delta P = P_1^\circ \cdot X_2 \Rightarrow X_2 = \frac{\Delta P}{P_1^\circ} = \frac{0,2}{32} = 6,25.10^{-3}$

(½) $X_2 = \frac{n_2}{n_1 + n_2}$ (½)

n_1 = nombre de mole du solvant $n_1 = \frac{1000}{18} = 55,5$ m

n_2 = nombre de mole du soluté A

$\frac{n_2}{55,56 + n_2} = 6,25.10^{-3} \Rightarrow n_2 = 0,349$ mol (½)

2/ $n_2 = \frac{m}{M} \Rightarrow M = \frac{m}{n_2} = \frac{20}{0,349} = \underline{\underline{57,30\ g}}$ (½)

LEBANESE UNIVERSITY
Faculty of Medical Sciences
Faculty of Dentistry

Duration: 1 h
September 20, 2010

Entrance Exam 2010-2011
Subject: Chemistry

Exercise I (9 pts)

A thermodynamic study shows that the following reaction has an enthalpy change $\Delta H° = -78$ kJ and an entropy change $\Delta S° = -202\ J.K^{-1}$ at $T = 305$ K

$$A + B_2 \rightleftharpoons AB_2$$

1) Calculate $\Delta G°$ and comment on its sign.

2) Write the relation that allows to calculate $\Delta S°$ knowing that of $\Delta S°_{298}$

3) Calculate the equilibrium constant at 305 K then calculate its value at 298 K assuming that $\Delta H°$ is constant in the given interval of temperature. Compare the values of the equilibrium constants and deduce the direction in which the equilibrium shifts

4) Deduce $\Delta G°$ at 298K

1) $\Delta G = \Delta H - T\Delta S = -78 - 305\,(-202\times10^{-3}) = -16,39\ Kj$ (1)

$\Delta G^\circ < 0 \Rightarrow$ la réaction est spontanée dans le sens direct (1/2)

2) $\Delta_r S^\circ_T = \Delta_r S^\circ_{298} + \int_{298}^{T} \Delta_r C_p \frac{dT}{T}$ (1)

3) $\Delta_r G^\circ = -RT\ln K \Rightarrow K = e^{-\frac{\Delta G^\circ}{RT}}$ (1) $= e^{\frac{16,39}{8,31\times10^{-3}\times305}} = 643,3$ (1/2)

$$\ln\frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ (1)

$$\Rightarrow \ln\frac{K_{298}}{K_{305}} = \frac{-78}{8.31\times10^{-3}}\left(\frac{1}{305} - \frac{1}{298}\right)$$ (1/2)

$$= \frac{-78000}{8,31}\left(\frac{298-305}{305\times298}\right)$$

$$= 0,723$$ (1/2)

$\Rightarrow \ln K_{298} = 7,19$

d'où $K_{298} = e^{7,19} = 1326$ (1/2)

$\Delta_r H^\circ < 0 \Rightarrow$ la diminution de la température déplace l'équilibre dans le sens exothermique $\Rightarrow$ dans le sens 1 (1)

4) $\Delta G^\circ_{298} = -RT\ln K_{298} = -8.31\times298\times\ln 1326 = -17,804\ Kj$ (1/2)

1) Correction devoir

1- $H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$ $\quad K_a = 6,2.10^{-8}$

$pK_a = 7,2$

Solution tampon formée par le couple H_2A / HA^-

(1) $pH = pK_a + \log \frac{[HA^-]}{[H_2A]} = pK_a + \log \frac{n_{HA^-}}{n_{H_2A}}$

$= 7,2 + \log \frac{0,03}{0,01} = \underline{7,68}$ (1)

2- $HA^- + H_3O^+ \longrightarrow H_2A + H_2O$ (1)

	HA^-	H_3O^+	H_2A
EI	0,03	0,005	0,01
EF	0,03-0,005	ε	0,01+0,005

$pH = pK_a + \log \frac{n_{HA^-}}{n_{H_2A}} = 7,2 + \log \frac{0,03-0,005}{0,01+0,005}$

$pH = \underline{7,42}$ (1)

3- $H_2A + HO^- \longrightarrow HA^- + H_2O$

	H_2A	HO^-	HA^-
EI	0,01	0,004	0,03
EF	0,01-0,004	ε	0,03+0,004

ΔpH négligé (1)

$pH = pK_a + \log \frac{n_{HA^-}}{n_{H_2A}} = 7,2 + \log \frac{0,03+0,004}{0,01-0,004}$

$pH = \underline{7,95}$ (1)

→ Suite

1) ordre 1 $\Rightarrow \underset{(1)}{\ln \frac{a}{a-x}} = kt \Rightarrow \ln \frac{0,1}{0,085} = K_1 \times 575 \Rightarrow K_1 = 2,8 \times 1$

(1) $\ln \frac{0,1}{0,074} = K_2 \times 1090 \Rightarrow K_2 = 2,75 \times$

$\ln \frac{0,1}{0,063} = K_3 \times 1720 \Rightarrow K_3 = 2,74$

$K_1 \simeq K_2 \simeq K_3 \Rightarrow$ l'ordre 1 est vérifié (1)

3

---

2) $K = \frac{K_1 + K_2 + K_3}{3} = 2,76 \times 10^{-4}\ s^{-1}$ (1)

ordre 1 $\Rightarrow t_{1/2} = \underset{(1)}{\frac{\ln 2}{K}} = \frac{0,69}{2,76 \times 10^{-4}} = 2500\ s$ $(1/2)$ $(1/2)$

4

---

3) Loi d'Arrhenius $\Rightarrow K = A e^{-\frac{E_a}{RT}}$ (1)

$\Rightarrow \ln K = \ln A - \frac{E_a}{RT}$

et $\ln K' = \ln A - \frac{E_a'}{RT}$

$\Rightarrow \ln \frac{K}{K'} = \frac{1}{RT}(E_a' - E_a)$

$\Rightarrow \ln \frac{K}{K'} = \frac{1}{8,31(27+273)}(100 - 125)$ (1)

$\Rightarrow \ln \frac{K}{K'} = -10,03$

$\Rightarrow \frac{K}{K'} = 4,41 \times 10^{-5}$

d'où $\frac{K'}{K} = 22653$ (1)

3

Exercice IV

A]

$3\times$ | $ClO^- + 2e^- + H_2O = Cl^- + 2HO^-$ (1/2)

$2\times$ | $CrO_2^- + 4HO^- = CrO_4^{2-} + 3e^- + 2H_2O$ (1/2)

$$3ClO^- + 2CrO_2^- + 2HO^- = 3Cl^- + 2CrO_4^{2-} + H_2O$$ (1/2)

1 1/2

B] 1) $Cr^{3+} + e^- = Cr^{2+}$

$$E_1 = E^\circ_{1(Cr^{3+}/Cr^{2+})} + \frac{0,059}{n} \log \frac{[Cr^{3+}]}{[Cr^{2+}]}$$ (1/2)

$$E_1 = -0,407 + \frac{0,059}{1} \log \frac{10^{-1}}{10^{-3}}$$

$$E_1 = \underline{-0,289V}$$ (1/2)

1

$V^{3+} + e^- = V^{2+}$

$$E_2 = E^\circ_{2(V^{3+}/V^{2+})} + \frac{0,059}{n} \log \frac{[V^{3+}]}{[V^{2+}]}$$ (1/2)

$$E_2 = -0,255 + 0,059 \log \frac{10^{-3}}{10^{-1}}$$

$$E_2 = \underline{-0,373V}$$ (1/2)

1

$E_1 > E_2$

2) $Cr^{3+} + V^{2+} \rightleftharpoons Cr^{2+} + V^{3+}$ (1/2) — 1/2

---

3) $E = E_1 - E_2 = -0,289 - (-0,373)$

$= \underline{0,084\,V}$ (1/2)

$k = 10^{\frac{n(E_1^\circ - E_2^\circ)}{0,059}} = 10^{\frac{1 \times (-0,152)}{0,059}}$ (1)

$= \underline{2,65 \cdot 10^{-3}}$ (1/2) — 2

$n_{e^- global} = 1$

$E_1^\circ - E_2^\circ = -0,407 - (-0,255) = -0,152$

1- $\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ (½)

$\Rightarrow \frac{1}{97,53 \times 10^{-9}} = 1,091 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right)$

$\Rightarrow n_2 = 4$ (½)

2- $E = \frac{hc}{\lambda} = hc R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ (½)

avec $n_1 = 1$ et $n_2 = \infty$

$\Rightarrow E = 6,626 \times 10^{-34} \times 3 \times 10^8 \times 1,091 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty} \right)$

$\Rightarrow E = 21,69 \times 10^{-19}$ J/ atome (½)

$\Rightarrow E = 130,64 \times 10^4$ J/mol soit 1306,4 KJ/mol (½)

3) (½) O_2 : $(6_{1s})^2 (6^*_{1s})^2 (6_{2s})^2 (6^*_{2s})^2 (6_{2p_z})^2 (\Pi_{2p_x})^2 (\Pi_{2p_y})^2 (\Pi^{*1}_{2p_x}) (\Pi^{*1}_{2p_y}) (6^*_{2p_z})$

(½) O_2^- : $(6_{1s})^2 (6^*_{1s})^2 (6_{2s})^2 (6^*_{2s})^2 (6_{2p_z})^2 (\Pi_{2p_y})^2 (\Pi_{2p_y})^2 (\Pi^{*}_{2p_x})^2 (\Pi^{*1}_{2p_y})$

(½) O_2^{2-} : $(6_{1s})^2 (6^*_{1s})^2 (6_{2s})^2 (6^*_{2s})^2 (6_{2p_z})^2 (\Pi_{2p_x})^2 (\Pi_{2p_y})^2 (\Pi^{*}_{2p_x})^2 (\Pi^{*}_{2p_y})^2$

) Indice de liaison : $n = \frac{1}{2}$ (nē liants − nē antiliants).

$n_{O_2} = 2$ (½) $n_{O_2^-} : 3/2$ (½) $n_{O_2^{2-}} = 1$ (½) (1 pt ton

) $E_{O_2^{2-}} < E_{O_2^-} < E_{O_2}$ (½)

Exercice VI — Propriétés colligatives

1/ $\Delta P = P_1^\circ \cdot X_2 \Rightarrow X_2 = \frac{\Delta P}{P_1^\circ} = \frac{0,2}{32} = 6,25.10^{-3}$

(½) $X_2 = \frac{n_2}{n_1 + n_2}$ (½)

n_1 = nombre de mole du solvant $n_1 = \frac{1000}{18} = 55,56$ mol

n_2 = nombre de mole du soluté A

$\frac{n_2}{55,56 + n_2} = 6,25.10^{-3} \Rightarrow n_2 = 0,349$ mol (½)

2/ $n_2 = \frac{m}{M} \Rightarrow M = \frac{m}{n_2} = \frac{20}{0,349} = \underline{\underline{57,30\ g}}$ (½)

UNIVERSITE LIBANAISE
Faculté des Sciences Médicales
Faculté de Médecine Dentaire

Durée : 1 h
12 septembre 2011

Concours d'entrée 2011-2012
Matière : Chimie

Exercice I (11 pts)

On considère la réaction suivante à 298 *K*:

$$2A(g) + B(g) \leftrightarrows 2C$$

	A(g)	B(g)	C(g)
ΔH_f^0 $(kJ.mol^{-1})$	– 296	0	– 395
S^0 $(J.mol^{-1}.K^{-1})$	248	205	256
C_p $(J.mol^{-1}.K^{-1})$	$40 + 42{,}6.10^{-3}\,T$	$29 + 13{,}6.10^{-3}\,T$	$50 + 45{,}0.10^{-3}\,T$

a. Calculer ΔU^0 de la réaction à 298 *K*

b. Calculer ΔG^0 de la réaction à 298 *K*

c. Calculer K_p à 298 *K*

d. Calculer ΔH^0 de la réaction à 798 K

On donne : R = 8,31 $J.mol^{-1}.K^{-1}$

Exercice II (10 pts)

On titre 10 mL d'une solution d'une dibase faible, notée B^{2-} ($1x10^{-1}$ $mol.L^{-1}$) avec une solution de HCl ($2x10^{-1}$ $mol.L^{-1}$).

On donne: $pK_{a1} = 4$ $pK_{a2} = 8$

a. Ecrire les équations des réactions de dosage

b. Calculer les volumes d'acide ajoutés au premier et au deuxième point d'équivalence

c. Déterminer les pH au premier et au deuxième points d'équivalence.

Exercice III (6 pts)

I- Le chloropropane se décompose selon la réaction à 398 ^0C :

$$C_3H_7Cl \rightarrow HCl + C_3H_6$$

Sachant que la constante de vitesse est égale à $0,37x10^{-4}\ s^{-1}$ à 398 ^0C

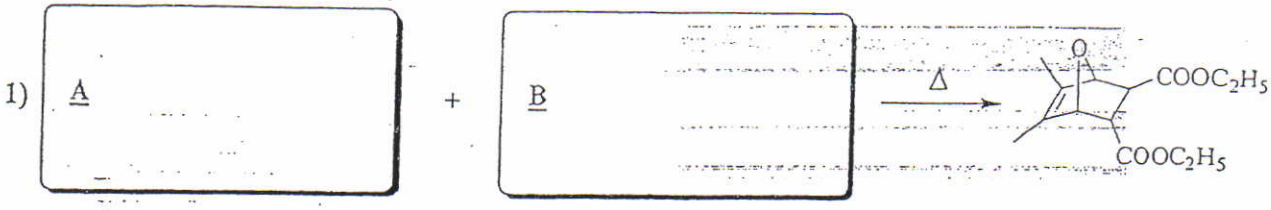
a. Ecrire la loi de vitesse de la réaction

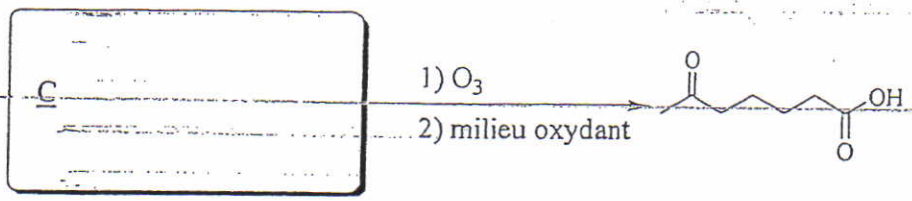
b. Déduire le temps de demi-réaction $t_{1/2}$

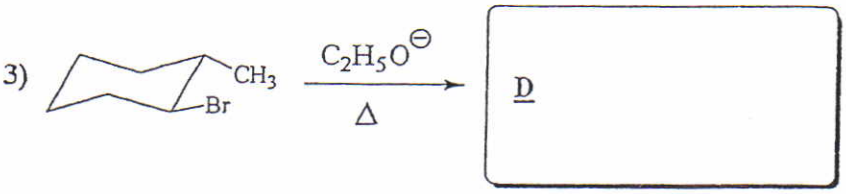
c. Calculer le temps au bout duquel il ne reste que 1/10 de la quantité initiale de chloropropane

Exercice 4:(2 points)

Compléter, sans mécanisme, les réactions suivantes:

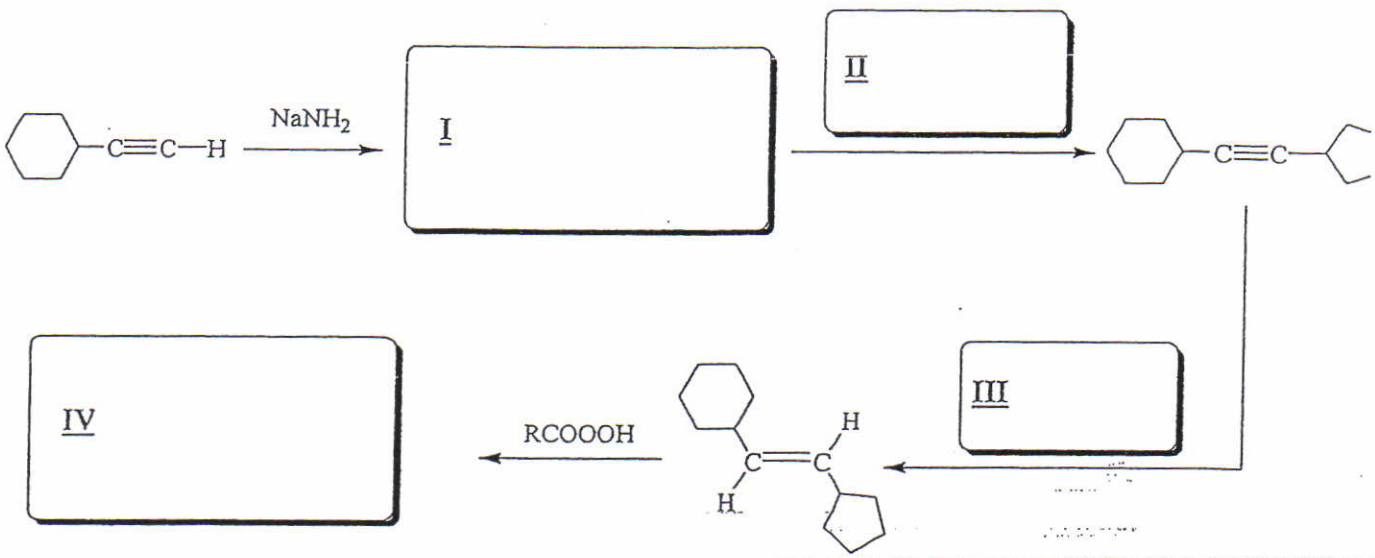
1) 

2) 

3) 

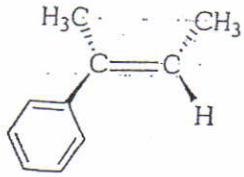
Exercice 5:(2 points)

Donner les structures chimiques des composés I, II, III et IV :



Exercice 6:(7 points)

On effectue la réaction suivante :



$\xrightarrow[\text{ou } Br_2/H_2O]{BrOH}$ ----------

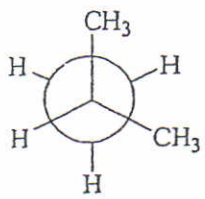
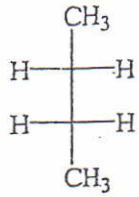
1) Quel est le type de cette réaction?

2) Donner le mécanisme détaillé de cette réaction.

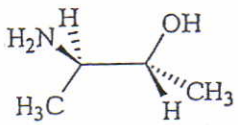
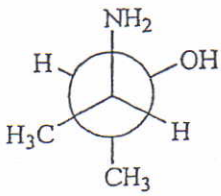
3) Préciser la configuration absolue des carbones asymétriques ainsi obtenus.

Exercice 7: (2 points)

Indiquer la relation qui existe entre les composés dans chacun des couples suivants:

1)  et 

Relation: ----------

2)  et 

Relation: ----------

UNIVERSITE LIBANAISE
Faculté de Pharmacie

Durée : 2 h
12 septembre 2011

Concours d'entrée 2010-2011

Matière : Chimie

Exercice I (11 pts)

On considère la réaction suivante à 298 *K*:

$$2A(g) + B(g) \leftrightarrows 2C$$

	A(g)	B(g)	C(g)
ΔH_f^0 $(kJ.mol^{-1})$	– 296	0	– 395
S^0 $(J.mol^{-1}.K^{-1})$	248	205	256
C_p	$40 + 42{,}6.10^{-3}\,T$	$29 + 13{,}6.10^{-3}\,T$	$50 + 45{,}0.10^{-3}\,T$

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b. Calculer ΔG^0 de la réaction à 298 *K*

c. Calculer K_p à 298 *K*

d. Calculer ΔH^0 de la réaction à 798 K

On donne : R = 8,31 $J.mol^{-1}.K^{-1}$

Exercice II (10 pts)

On titre 10 mL d'une solution d'une dibase faible, notée B^{2-} ($1x10^{-1}$ $mol.L^{-1}$) avec une solution de HCl ($2x10^{-1}$ $mol.L^{-1}$).

On donne: $pK_{a1} = 4$ $pK_{a2} = 8$

a. Ecrire les équations des réactions de dosage

b. Calculer les volumes d'acide ajoutés au premier et au deuxième point d'équivalence

c. Déterminer les pH au premier et au deuxième points d'équivalence.

Exercice III (6 pts)

I- Le chloropropane se décompose selon la réaction à 398 ^0C :

$$C_3H_7Cl \rightarrow HCl + C_3H_6$$

Sachant que la constante de vitesse est égale à $0,37x10^{-4}\ s^{-1}$ à 398 ^0C

a. Ecrire la loi de vitesse de la réaction

b. Déduire le temps de demi-réaction $t_{1/2}$

c. Calculer le temps au bout duquel il ne reste que 1/10 de la quantité initiale de chloropropane

Exercice IV (9 pts)

Une pile électrochimique est composée des deux demi-piles suivantes (à 298 K):

$Fe^{3+} + e^- \leftrightarrows Fe^{2+}$ $\quad E^0 = 0.77\ V$

$Sn^{2+} + 2e^- \leftrightarrows Sn$ $\quad E^0 = -0.13\ V$

a. Ecrire l'équation globale de la reaction

b. Calculer la f.é.m standard de la pile

c. Calculer la constante d'équilibre de la réaction

d. Calculer l'enthalpie standard de la réaction

libre

e. Quelle serait la f.é.m de la pile si $[Fe^{3+}] = 1\ mol.L^{-1}$ et $[Sn^{2+}] = 0.001\ mol.L^{-1}$

On donne : 1 Faraday = 96500 C

Exercice V (4 pts)

a. Calculer l'énergie d'ionisation d'un atome d'hydrogène dont l'électron se trouve sur le niveau excité n = 3

b. Calculer la longueur d'onde associée à cette énergie

c. Déduire la valeur de la constante de Rydberg R_H.

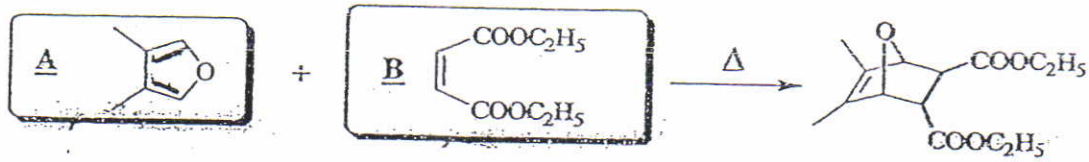
On donne: $h = 6.626.10^{-34}\ J.s$; 1 e.V = $1,6.10^{-19}$ J ; $c = 3.10^{8}\ m.s^{-1}$

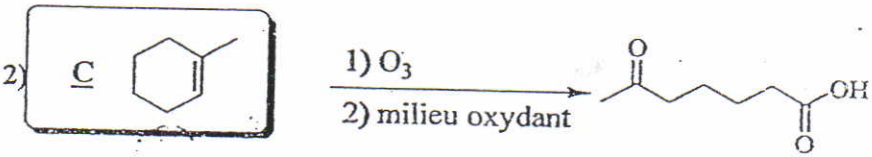
2011/2012

Exercice 1 (5 points)

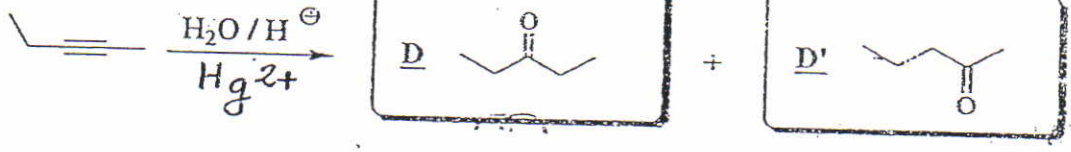
Concours Pharmacie / 2011 - 2012

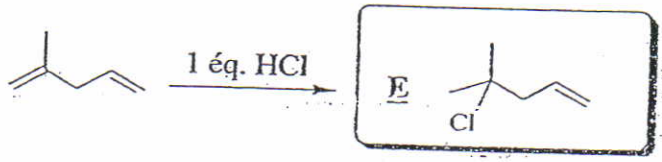
Compléter, sans mécanisme, les réactions suivantes:

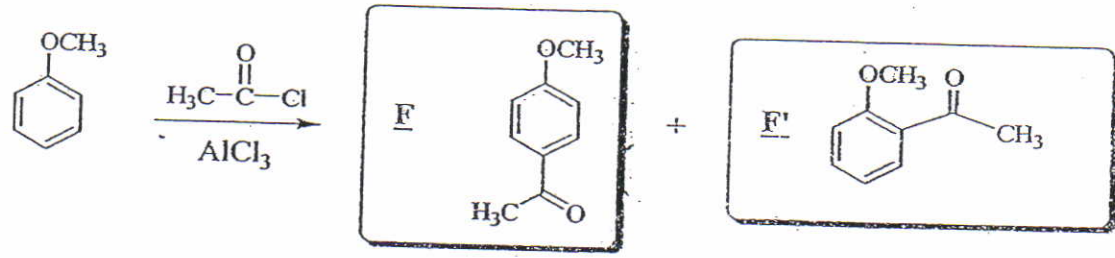
1) 

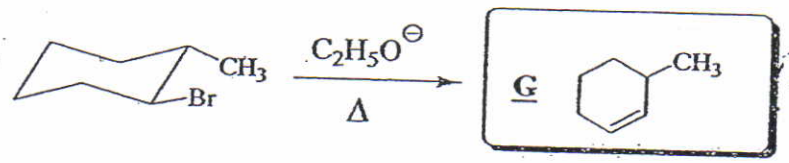
2) 

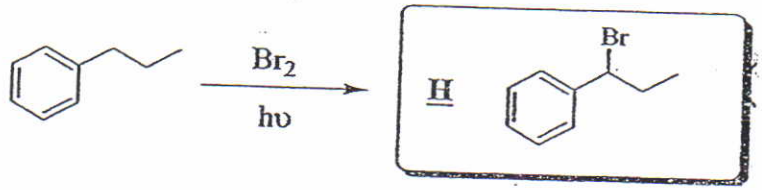
Chimie organique
Durée : 40 min

3) 

4) 

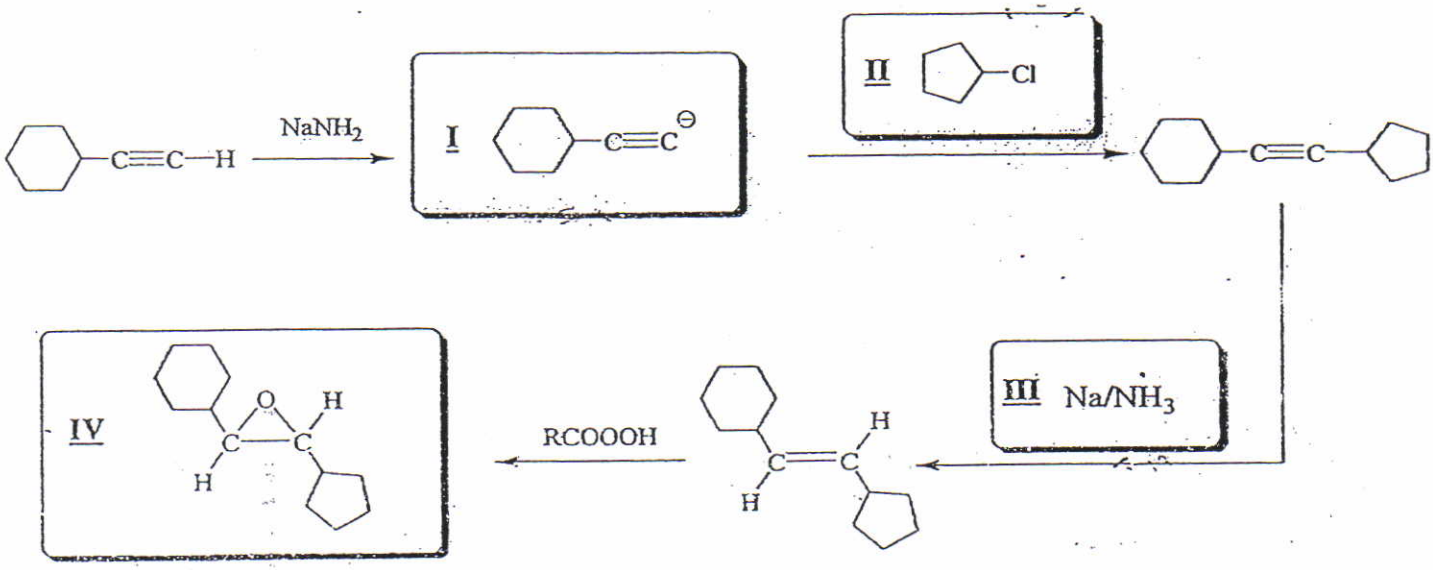
5) 

6) 

7) 

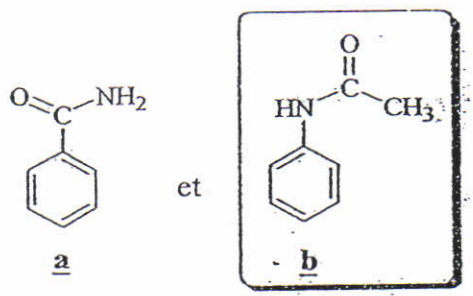
Exercice 2 (2 points)

Donner les structures chimiques des composés I, II, III et IV :



Exercice 3 (2 points)

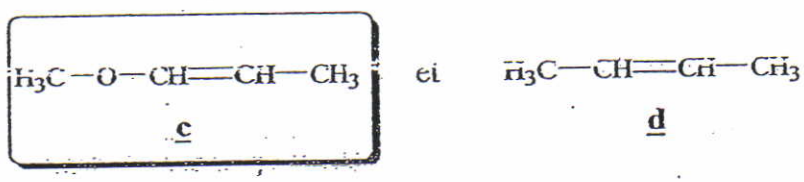
a) Indiquer le produit le plus réactif vis à vis d'une réaction de substitution électrophile.



a et b

b

b) Indiquer le produit le plus réactif vis à vis d'une réaction d'addition de HCl:



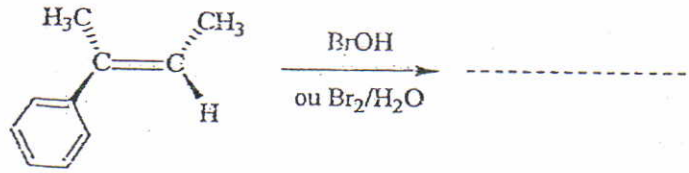
c et d

c

77

Exercice 4 (8 points)

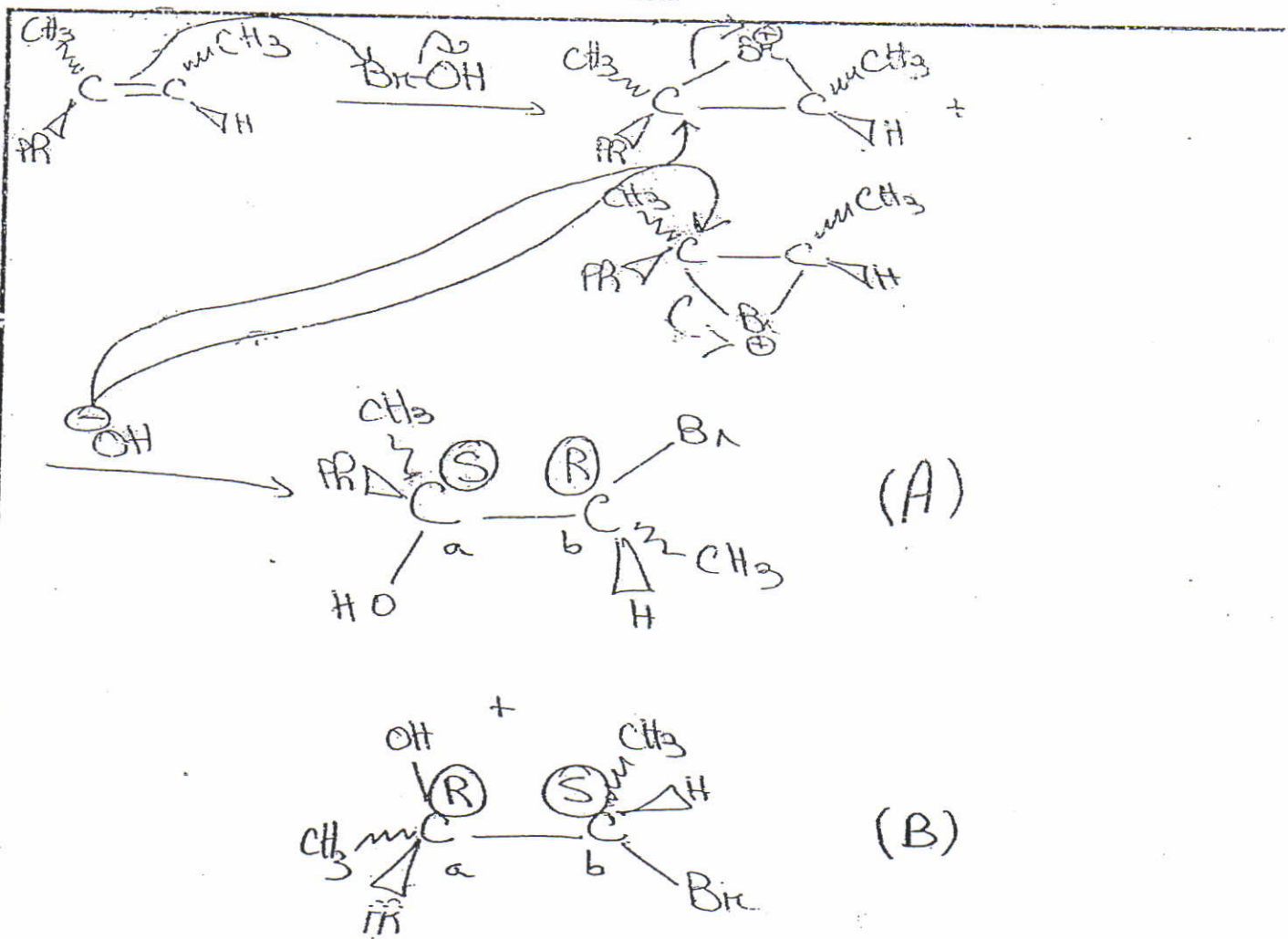
On effectue la réaction suivante :



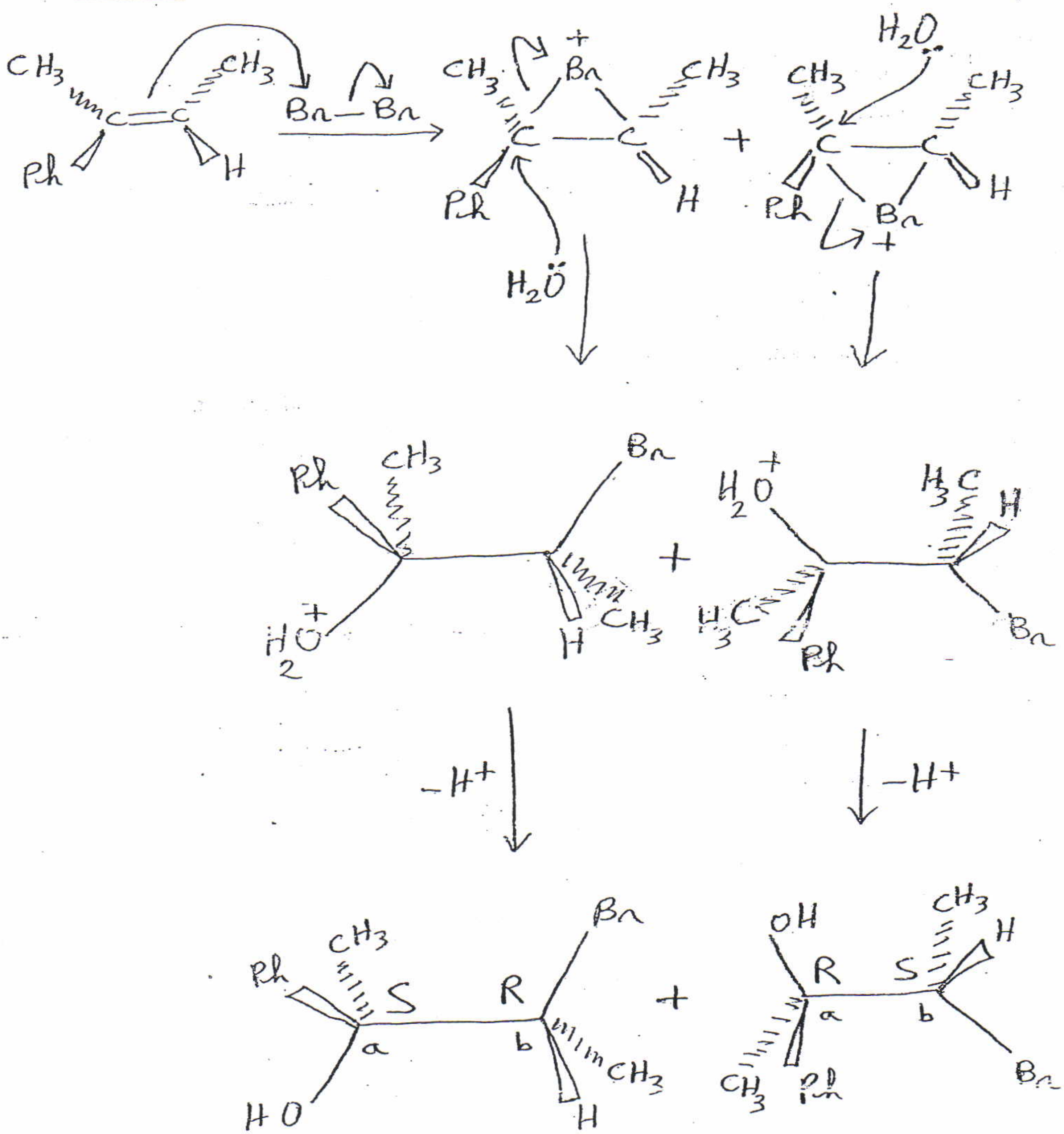
1) Quel est le type de cette réaction?

Addition électrophile

2) Donner le mécanisme détaillé de cette réaction.



Ou :



CH3
CH3
Ph
H
Br—Br
+
Br
CH3
CH3
C
C
Ph
H
H2O
+
H2O
CH3
CH3
Ph
Br
H
Ph
CH3
Br
H2O
H
CH3
+
H2O
H3C
H
H3C
Ph
Br
−H+
−H+
Ph
CH3
S
R
Br
HO
a
b
CH3
H
+
OH
R
S
CH3
H
a
b
CH3
Ph
Br

(A)

(B)

3) Préciser la configuration absolue des carbones asymétriques ainsi obtenus.

A : $C_a \rightarrow S$, $C_b \rightarrow R$

B : $C_a \rightarrow R$, $C_b \rightarrow S$

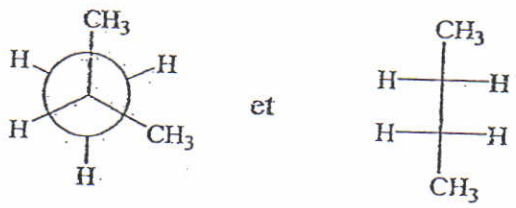
4) Le produit obtenu est-il optiquement actif? Justifier brièvement votre réponse.

Optiquement inactif

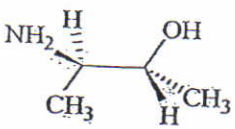
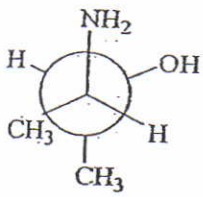
Mélange racémique

Exercice 5 (3 points)

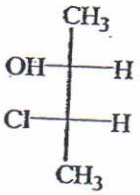
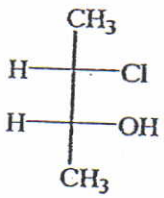
Indiquer la relation qui existe entre les composés dans chacun des couples suivants:

1)  et

Relation: isomères de structure

2)  et 

Relation: énantiomères

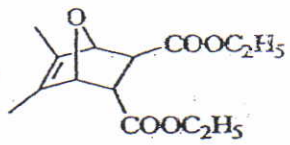
3)  et 

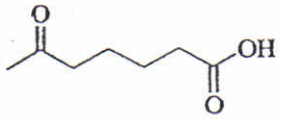
Relation: identiques

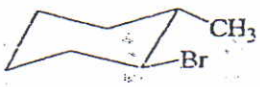
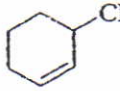
Exercice 1 (2 points)

Concours Médecine et Médecine Dentaire 2011-2012

Compléter, sans mécanisme, les réactions suivantes:

1) A + B ($COOC_2H_5$, $COOC_2H_5$) $\xrightarrow{\Delta}$ 

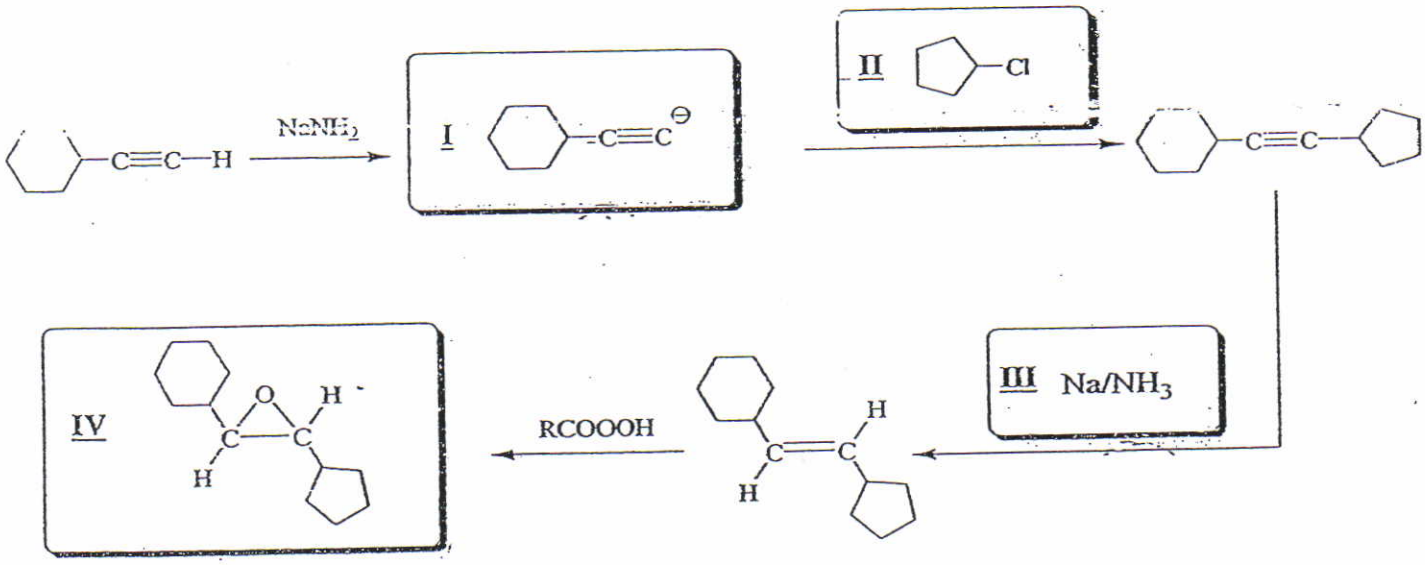
2) C $\xrightarrow[2)\ \text{milieu oxydant}]{1)\ O_3}$ 

3)  $\xrightarrow[\Delta]{C_2H_5O^{\ominus}}$ D ()

Chimie organique
Durée : 20 min

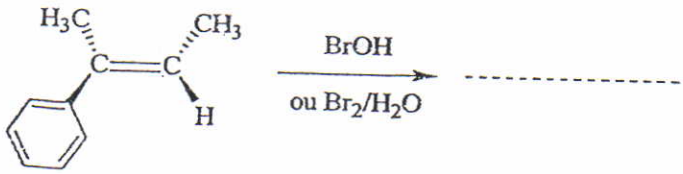
Exercice 2 (2 points)

Donner les structures chimiques des composés I, II, III et IV :



Exercice 3 (7 points)

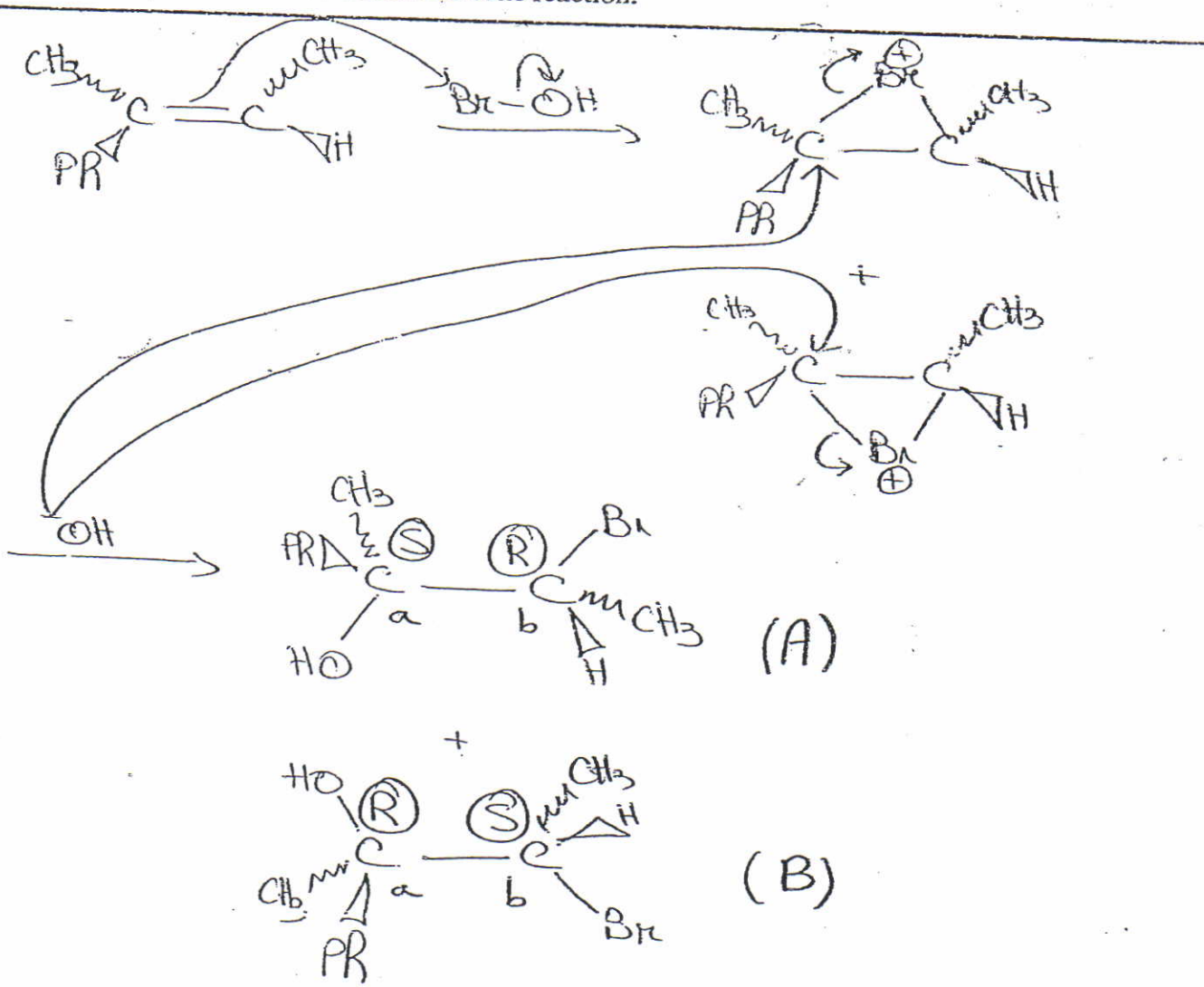
On effectue la réaction suivante :



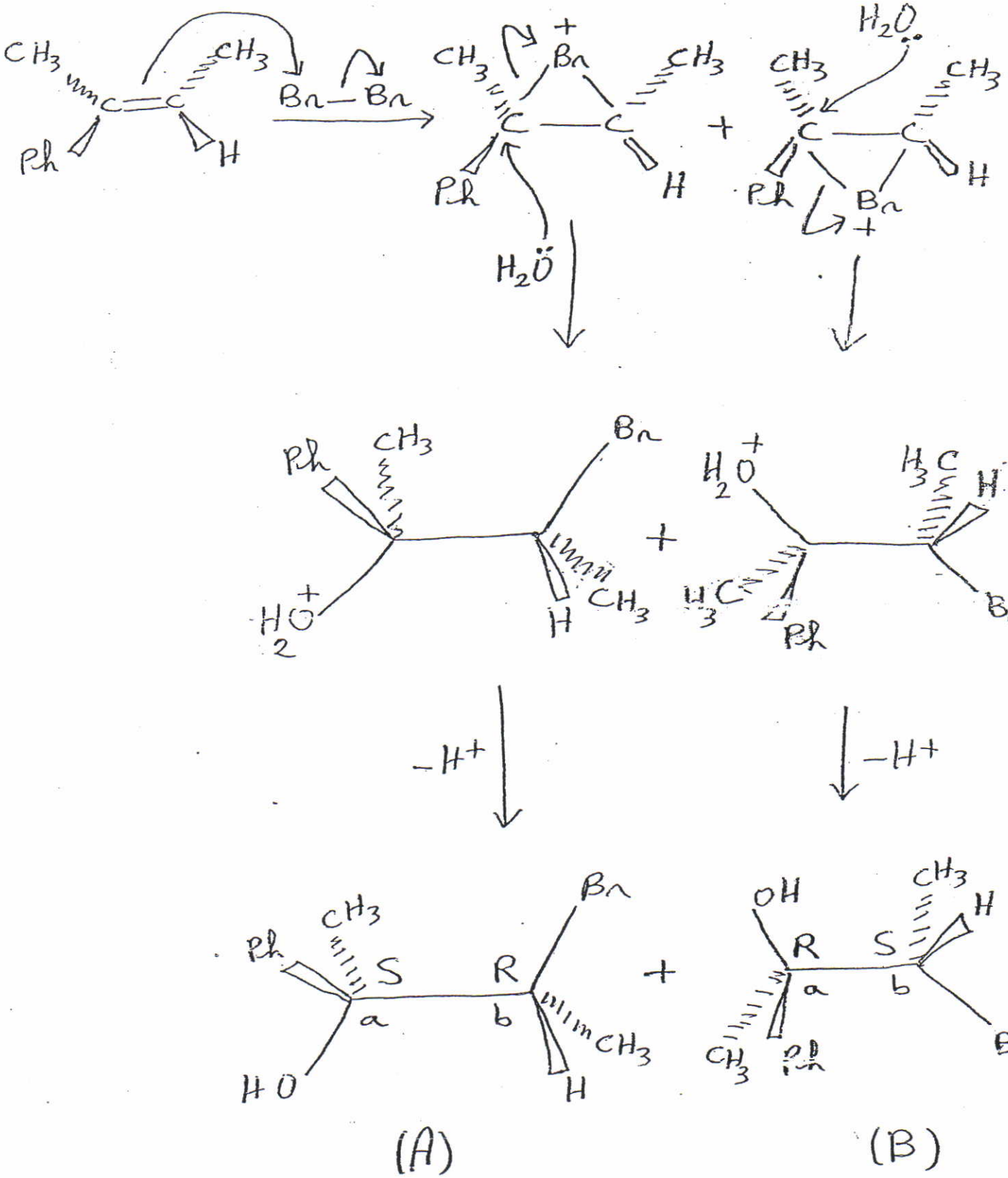
1) Quel est le type de cette réaction?

Addition électrophile

2) Donner le mécanisme détaillé de cette réaction.



Ou:



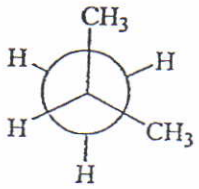
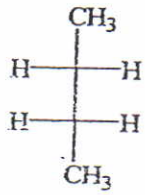
3) Préciser la configuration absolue des carbones asymétriques ainsi obtenus.

A: $C_a \rightarrow S$, $C_b \rightarrow R$

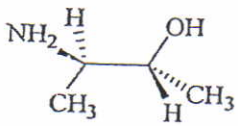
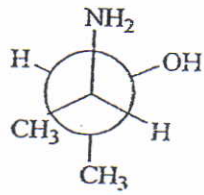
B: $C_a \rightarrow R$, $C_b \rightarrow S$

Exercice 4 (2 points)

Indiquer la relation qui existe entre les composés dans chacun des couples suivants:

1)  et 

Relation: isomères de structure

2)  et 

Relation: énantiomères

I)

Dr. Kamal HARIRI

a- $\Delta U^\circ = \Delta H^\circ - \Delta n RT$

$\Delta n = 2 - 3 = -1$.

$\Delta H^\circ_r = 2\,\Delta_f H^\circ(C) - 2\,\Delta H^\circ_f(A) - \Delta H^\circ_f(B)$

$= 2(-395) - 2(-296) - 0 = -198\ kJ = -198 \times 10^3\ J$.

$\Delta U^\circ = -198 \times 10^3 (-1) \times 8{,}31 \times 298 = \boxed{195{,}52\ kJ.}$

b- $\Delta_r G^\circ_{298} = \Delta H^\circ_r - T\Delta_r S^\circ_{298}$

$\Delta_r S^\circ_{298} = 2S^\circ(C) - 2S^\circ(A) - S^\circ(B)$

$= 2(256) - 2(248) - 205 = \boxed{-189\ J.mol^{-1}k^{-1}}$

$\Delta_r G^\circ_{298} = -198 \times 10^3 - 298(-189) = -141678\ J = \boxed{-141{,}678\ kJ.}$

c- $k_p = e^{-\frac{\Delta G^\circ}{RT}} \Rightarrow k_p = e^{\frac{141678}{8{,}31 \cdot 298}} = e^{57{,}21} \Rightarrow \boxed{k_p = 7{,}0265 \times 10^{24}}$

1- $\Delta_r H^\circ_{798} = \Delta_r H^\circ_{298} + \int_{298}^{798} \Delta_r C_p\, dT$

$\Delta_r C_p = 2C_p(C) - 2C_p(A) - C_p(C)$

$\Delta_r C_p = 2(50 + 45{,}0 \times 10^{-3} T) - 2(40 + 42{,}6 \times 10^{-3} T) - (29 + 13{,}6 \times 10^{-3} T)$

$\Delta_r C_p = -9 - 8{,}8 \times 10^{-3} T$

$\Delta_r H^\circ_{798} = -198 \cdot 10^3 + \int_{298}^{798} (-9 - 8{,}8 \cdot 10^{-3} T)\, dT$

$\Delta_r H^\circ_{798} = -198 \times 10^3 - 9(798 - 298) - \frac{1}{2}(8{,}8 \times 10^{-3})\left[(798)^2 - (298)^2\right]$

$\boxed{\Delta_r H^\circ_{798} = -204911{,}2\ J = 204{,}9\ kJ}$

Exercice II

(10 points)

a) $B^{2-} + H_3O^+ \longrightarrow HB^- + H_2O$

$HB^- + H_3O^+ \longrightarrow H_2B + H_2O$

b) $C_a V_{a\acute{e}q1} = C_b V_b \Rightarrow V_{a\acute{e}q1} = \dfrac{C_b V_b}{C_a} = \dfrac{10^{-1}.10}{2.10^{-1}} = 5\ mL$

$C_a V_{a\acute{e}q2} = 2 C_b V_b$ ou $V_{a\acute{e}q2} = 2 V_{a\acute{e}q1} = 2 \times 5 = 10\ mL$

$V_{a\acute{e}q2} = \dfrac{2 C_b V_b}{C_a} = \dfrac{2.10^{-1}.10}{2.10^{-1}} = \underline{10\ mL}$

c) - pH 1ère équivalence

le pH est donné par HB^- espèce ampholyte.

$pH = \frac{1}{2}(pK_{a_1} + pK_{a_2}) = \frac{1}{2}(4+8) = \underline{6}$

- pH 2ème équivalence

le pH est donné par le diacide faible H_2B

$Ka_1 \gg 100\, Ka_2$

$pK_{a_1} < pK_{a_2} - 2$, le pH est donné par la 1ère acidité seulement

Calcul de C_a': Concentration de H_2B

$$C_a' = \frac{C_b V_b}{V_{a\acute{e}q2} + V_b} = \frac{10^{-1}.10.10^{-3}}{(10+10).10^{-3}} = 5.10^{-2}\ mol.L^{-1}$$

$pK_{a_1} - p C_a' = 4 - (-\log 5.10^{-2}) = 2,7 > 2$

$pH = \frac{1}{2}(pK_{a_1} + p C_a') = \frac{1}{2}(4 - \log 5.10^{-2}) = \underline{2,65}$

$\underline{(2,65)}$

Exercice III

- Puisque $t_{1/2}$ est en s^{-1} $\Rightarrow$ la réaction est du 1er ordre

$\Rightarrow v = k [C_3H_7Cl] = -\frac{d}{dt}[C_3H_3Cl]$

- $t_{1/2} = \frac{\ln 2}{ak} = \frac{0,693}{1 \times 0,37 \times 10^{-4}} = 18729,73\ s$

- $\ln \frac{C_0}{C_0 - x} = akt \Rightarrow t = \frac{1}{ak} \ln 10$

$\Rightarrow t = \frac{1}{1 \times 0,37 \times 10^{-4}} \times \ln 10 = 6,22 \cdot 10^4\ s$

IV) a) $Sn + 2Fe^{3+} \longrightarrow Sn^{2+} + 2Fe^{2+}$

b) $\Delta E^\circ = E^\circ_{cathode} - E^\circ_{anode} = 0,77 - (-0,13) = 0,9V$

c) $K = 10^{\frac{n\Delta E^\circ}{0,06}}$

$K = 10^{\frac{2 \times 0,9}{0,06}} = 3,22 \times 10^{30}$

d) $\Delta G^\circ = -nF\Delta E^\circ = -2 \times 96500 \times 0,9$

$\Delta G^\circ = -173700\ J.mol^{-1}$

e) $\Delta E = \Delta E^\circ - \frac{0,06}{n} \log K$

$\Delta E = \Delta E^\circ - \frac{0,06}{2} \log \frac{[Sn^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$

$[Fe^{3+}] = 1M$; $[Sn^{2+}] = \frac{1}{2}[Fe^{2+}] = 10^{-3}M$

$\Delta E = 0,9 - 0,03 \log \frac{10^{-3}(2.10^{-3})^2}{1}$

$\Delta E = 1,15V$

Exercice II

4 points

a- $E_I = 0 - \left(-\frac{13.6}{n^2}\right) = \frac{13.6}{9} = 1,51\ eV = 2,41 \times 10^{-19}\ J$

b- $E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E} = \frac{6,626 \times 10^{-34} \times 3 \times 10^{8}}{2,41 \times 10^{-19}} = 8,248 \times 10^{-7}\ m$

c- $\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2}\right) = \frac{R_H}{9}$

$\Rightarrow R_H = \frac{9}{\lambda} = \frac{9}{8,248 \times 10^{-7}} = 1,09 \times 10^{7}\ m^{-1}$