



SEMI-FINALS: Problems

Dear students,

We congratulate you for your participation in the Chemistry Olympiad and we wish you every success in this second round as well as in your studies and in all your future endeavours. We also congratulate you on having passed the first test, which allows you today to tackle the "Problems" test. **Before beginning this test, read the following carefully.**

You will find attached 4 problems. The topics covered by these questions are: general chemistry, stoichiometry, pH, redox and organic chemistry.

You have **two hours** to answer all questions. You can use a non-programmable calculator, but you must not be in possession of any other documentation.

Indicate your name and high school at the beginning of each question. Answer each problem on the sheet (front and back, if necessary) where the statement appears. **Clearly state your reasoning and calculations.** Justify your answers and **indicate the units** to the final answers. The last sheet is a draft sheet that will not be considered for the evaluation. Detach the first two sheets and keep them for reference.

Following the evaluation of this second event, the 12 best students will be invited to participate in a final (practical) test, which will take place on **Wednesday, April 24th, 2019 at 14h00 in the laboratories at the Limpertsberg site of the University of Luxembourg.** This final exam will select the four winners of the National Chemistry Olympiad, who will make up the Luxembourgish team for the 51st IChO in Paris, from 21 to 30 July 2019. More information on <http://icho.olympiades.lu/>.

The results of this second event will be taken into account for the ranking of the four finalists!!!

Wishing you a good job, please believe in our best feelings.
The organizers of the Chemistry Olympiad

Detach and keep for your information



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Éducation nationale,
de l'Enfance et de la Jeunesse



UNIVERSITÉ DU
LUXEMBOURG



Fonds National de la
Recherche Luxembourg



FVEMT
FONDATION VEUVE
EMILE METZ-TESCH



andré & henriette losch
fondatioun

Natural constants

(You may detach this sheet if necessary)



TABLEAU PÉRIODIQUE DES ÉLÉMENTS

1 I a												13 14 15 16 17 III a IV a V a VI a VII a					18 VIII a	
1,01		masse atomique relative										A_r						4,00
H	2											X	élément					He
1	II a											Z						2
6,94	9,01											10,81	12,01	14,01	16,00	19,00	20,18	
Li	Be											B	C	N	O	F	Ne	
3	4											5	6	7	8	9	10	
22,99	24,31											26,98	28,09	30,97	32,07	35,45	39,95	
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar	
11	12	III b	IV b	V b	VI b	VII b	VIII b			I b	II b	13	14	15	16	17	18	
39,10	40,08	44,96	47,88	50,94	52,00	54,94	55,85	58,93	58,69	63,55	65,39	69,72	72,61	74,92	78,96	79,90	83,80	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
85,47	87,62	88,91	91,22	92,91	95,94		101,07	102,91	106,42	107,87	112,41	114,82	118,71	121,75	127,60	126,90	131,29	
Rb	Sr	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
132,91	137,33	(1)	174,97	178,49	180,95	183,9	186,21	190,21	192,22	195,08	196,97	200,59	204,38	207,21	208,98			
Cs	Ba	57 -	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po*	At*	Rn*
55	56	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Fr*	Ra*	(2)	Lr*	Rf*	Db*	Sg*	Bh*	Hs*	Mt*	Ds*	Rg*	Cn*	Nh*	Fl*	Mc*	Lv*	Ts*	Og*
87	88	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118

1) Lanthanides	138,92	140,12	140,91	144,24		150,36	151,97	157,25	158,93	162,50	164,93	167,26	168,93	173,04
	La	Ce	Pr	Nd	Pm*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
	57	58	59	60	61	62	63	64	65	66	67	68	69	70
2) Actinides		232,04	231,04	238,03										
	Ac*	Th	Pa	U	Np*	Pu*	Am*	Cm*	Bk*	Cf*	Es*	Fm*	Md*	No*
	89	90	91	92	93	94	95	96	97	98	99	100	101	102

* Eléments n'ayant pas de nucléide (isotope) de durée suffisamment longue et n'ayant donc pas une composition terrestre caractéristique.

Constants

$$R = 8,31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$1F = 9,65 \times 10^4 \text{ C mol}^{-1}$$

$$R = 8,21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$N_A = 6,02 \times 10^{23} \text{ mol}^{-1}$$

Volume of one mole of an ideal gaz at 273 K and 101 325 Pa : $22,4 \text{ dm}^3 \text{ mol}^{-1}$ (L mol^{-1})

Simplified formulae for the calculations of pH :

Strong acid	Weak acid	Strong base	Weak base
$pH = -\log c_{acide}$	$pH = \frac{1}{2}(pK_a - \log c_{acide})$	$pH = 14 + \log c_{base}$	$pH = 14 - \frac{1}{2}(pK_B - \log c_{base})$

Buffer mix : $pH = pK_a + \log \frac{c_{base}}{c_{acide}}$

A 25 °C : $K_w = K_{H_2O} = [H_3O^+] \cdot [OH^-] = 1,0 \cdot 10^{-14}$



Name :

First name :

School :

Problem I : Batteries

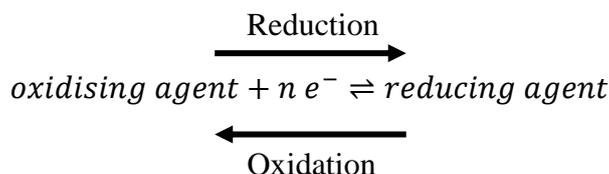
1a	1b	1c	1d	1e	1f	1g	Total Problem I
3	2	2	2	2	4	4	19

Introduction to the theory:

An oxidising agent is a chemical species capable of capturing at least one electron.

A reducing agent is a chemical species capable of yielding or giving up at least one electron.

An oxidizing / reducing pair (Ox / Red) consists of a conjugated oxidising agent and reducing agent which can exchange electrons according to the oxidation-reduction half-equation:



A redox reaction involves an electron transfer between two oxidation-reduction pairs. The reducing agent of an redox pair (Ox1 / Red1) yields electrons to the oxidising agent of another redox pair (Ox2 / Red2).

An electro-chemical cell is a generator that transforms the chemical energy provided by a spontaneous redox reaction into electrical energy.

If a battery discharges for a time Δt before being used, then it has delivered a quantity of electricity (Q in Coulomb) corresponding to:

$$Q = I \times \Delta t = n F$$

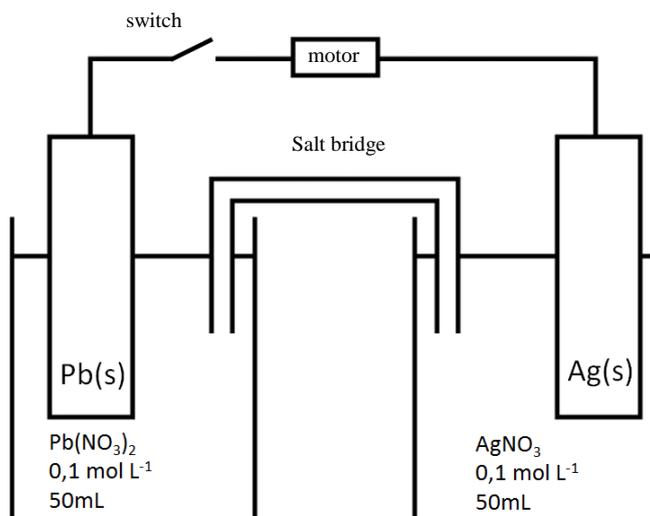
Where :

I is the current delivered by the battery

n is the number of moles of electrons exchanged throughout the reaction

F is the Faraday constant which is : $9,65 \times 10^4 \text{ C mol}^{-1}$.

A chemist with silver and lead metal electrodes and salt solutions of these metals wants to experiment with an electric battery and sets up the following electrochemical cell :



Some pairs of the redox pairs comparative cell values are shown in the table below :

Ag^+ / Ag	strongest oxidising agent
$2 \text{H}^+ / \text{H}_2$	
$\text{Pb}^{2+} / \text{Pb}$	strongest reducing agent

- a) Write the balanced equation for the redox reaction that occurs when the switch in the above diagram is closed.

- b) When the switch is closed, which electrode has oxidation occurring ?

Ag	Pb
----	----

- c) In which direction do the electrons move through the external circuit?

From Ag to Pb	From Pb to Ag
---------------	---------------

- d) When the battery has been running for a while, which electrode will gain mass ?

Ag	Pb
----	----

- e) What is the quantity of electricity that flows through the battery when it runs for one hour with a constant current of 65 mA?

- f) What will be the theoretical mass variation (shown as Δm) experienced by the lead electrode after the battery has been left running for the same period of time.

- g) What will be the final concentration of Pb^{2+} ions?



Name :

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Problem II : Organics

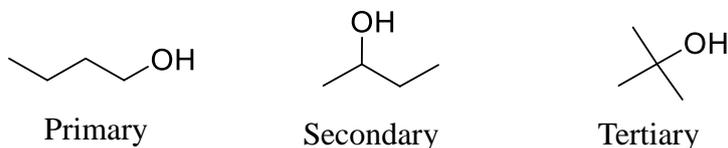
2a	2b	2c	2di	2dii	2diii	2e	Total Problem II
4	4	4	4	4	4	5	29

Note: It is not necessary to have studied organic chemistry in depth to answer this question. Theoretical information for answering the sub-questions are given in the statement.

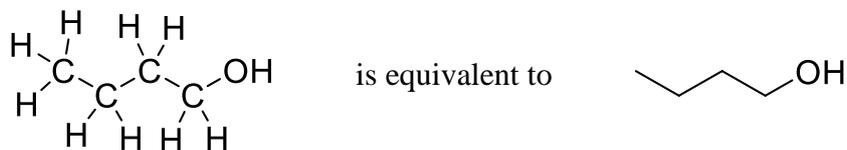
In chemistry, an alcohol is an organic compound of which one of the carbon atoms is linked to a hydroxyl functional group -OH. Depending on the nature of the carbon carrying the alcohol functional group, they are classified as:

- Primary alcohols whose carbon atom is carrying two hydrogen atoms.
- Secondary alcohols in which the carbon atom carries a single hydrogen atom.
- Tertiary alcohols in which the carbon atom does not carry any hydrogen atoms.

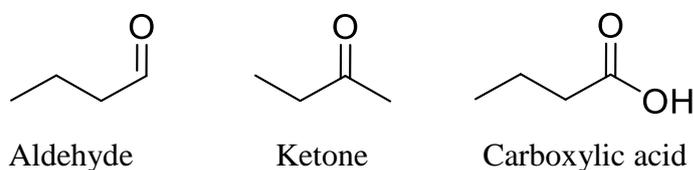
Examples are shown below.



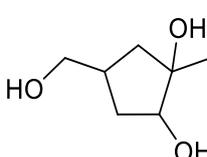
Note that in the skeleton (topological) formula shown above all of the hydrogen atoms are omitted and only the carbon atoms are represented. The two diagrams below show the same compound :



Oxidation is a common reaction within alcohols. While primary alcohols oxidize readily to form aldehydes and secondary alcohols oxidize to form ketones, tertiary alcohols do not undergo any form of oxidation. The primary alcohol conversion to aldehydes can be further oxidized to form carboxylic acids. Usually, this step proceeds rapidly and the intermediate aldehyde cannot be easily isolated.



- a) a) Circle the alcohol functional groups in the following compound and indicate whether they are primary, secondary or tertiary. Draw the completed product of (total) oxidation for this compound.

Initial structure	Product of oxidation
	

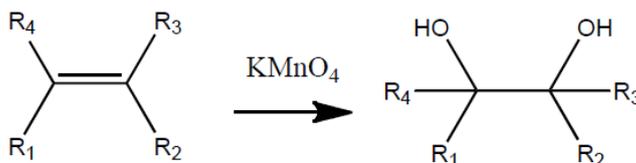
There are a number of qualitative tests that can be performed to determine the presence of certain functional groups.

Tollens reagent

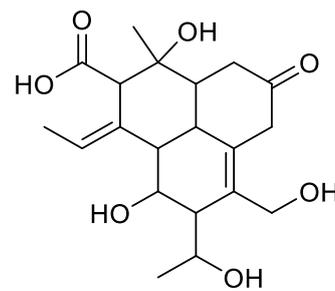
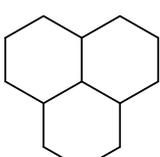
An ammonia solution of silver nitrate (Tollens reagent) is commonly used for the oxidation of aldehydes. A positive test is characterized by the precipitation of silver to form a "silver mirror". Due to the high reactivity of the aldehydes, only these functional groups can be easily detected using this method.

Potassium permanganate

Acidified and heated potassium permanganate is commonly used to oxidize alcohols, but it also causes the formation of diols on an alkene bond, as indicated below. It is assumed that a solution of the acidified potassium permanganate will oxidize all the primary alcohols and aldehydes to carboxylic acids and that the $C = C$ bonds will form diols (followed by further oxidation, if possible). Note that "R" represents the rest of the molecule. Normally, the permanganate ion is violet, but it is decolorized during the reduction because it leaves behind the colourless Mn^{2+} ions.

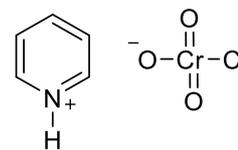


- b) Draw the product when Compound A (shown below) is treated with an excess of acidified potassium permanganate. (A partial structure has been drawn for you.)

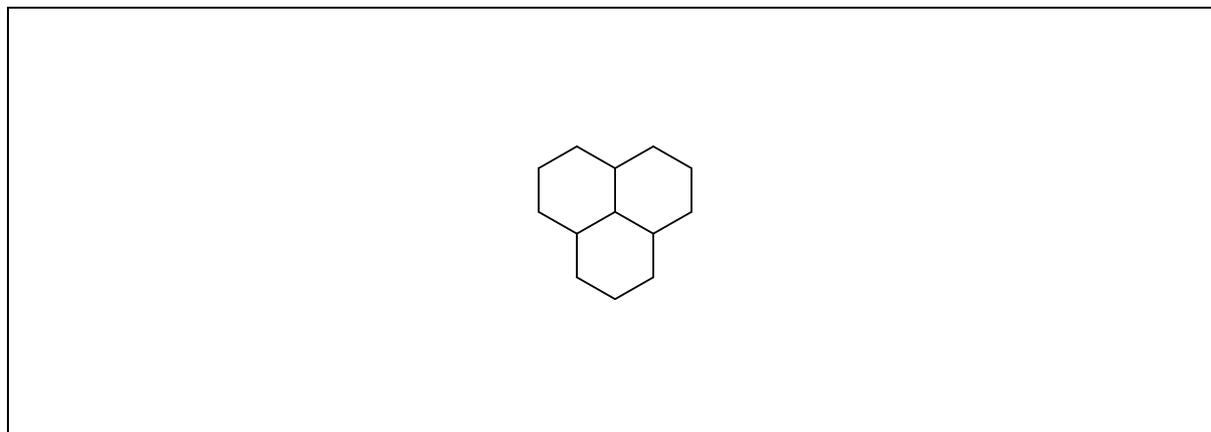
 <p>A</p>	
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Pyridinium Chlorochromate (PCC)

Pyridinium chlorochromate has an advantage over the use of potassium permanganate because it can act in a more selective way. This reagent does not oxidize aldehydes, ketones or alkenes, but only alcohols. The structure of the PCC is illustrated here. The PCC is red-orange and its reduced form is green.

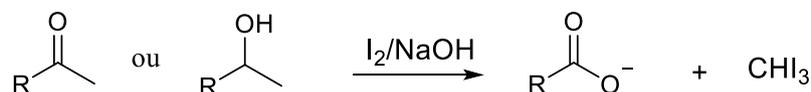


- c) Draw the product formed when Compound A is treated with PCC. (A partial structure has been drawn for you.)



Iodoform

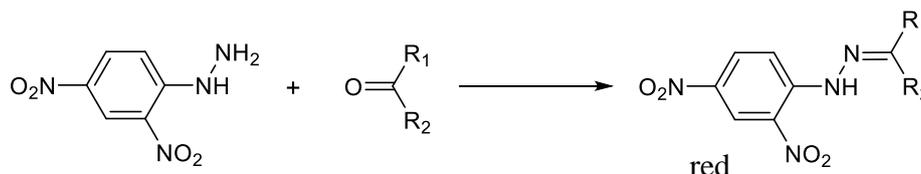
The iodoform test is commonly used to detect the presence of methyl ketone and methylated secondary alcohols, including ethanol and ethanal. When adding I_2 (in a basic solution), the alcohol is oxidized to ketone which then reacts to produce the carboxylate ion and a yellow precipitate of iodoform (CHI_3). Note that the addition of iodine on an alkene bond does not occur under these conditions.



The iodine solution generally has a brown-red colour which fades as the reaction progresses, allowing the yellow colour of the iodoform to appear. In addition, I_2 oxidizes all primary alcohols and aldehydes to carboxylic acids as well as secondary alcohols to ketones.

2,4-dinitrophenylhydrazine (DNPH)

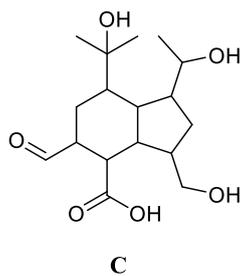
DNPH (also called Brady's reagent) is used to detect the presence of aldehydes and ketones, which is confirmed by the presence of a red precipitate. The equation of the reaction that occurs is as follows:



Identification of functional groups

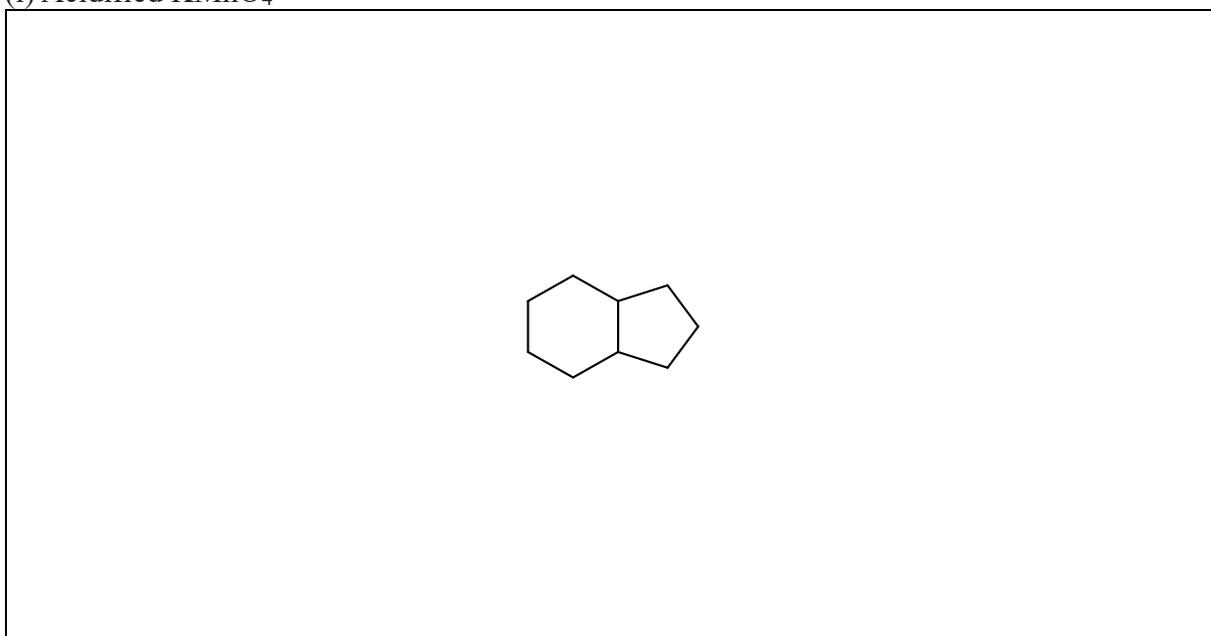
The qualitative tests above can be used in combination to identify the presence of the different functional groups within a compound.

d) A sample of compound C was oxidized, followed by treatment with DNPH.

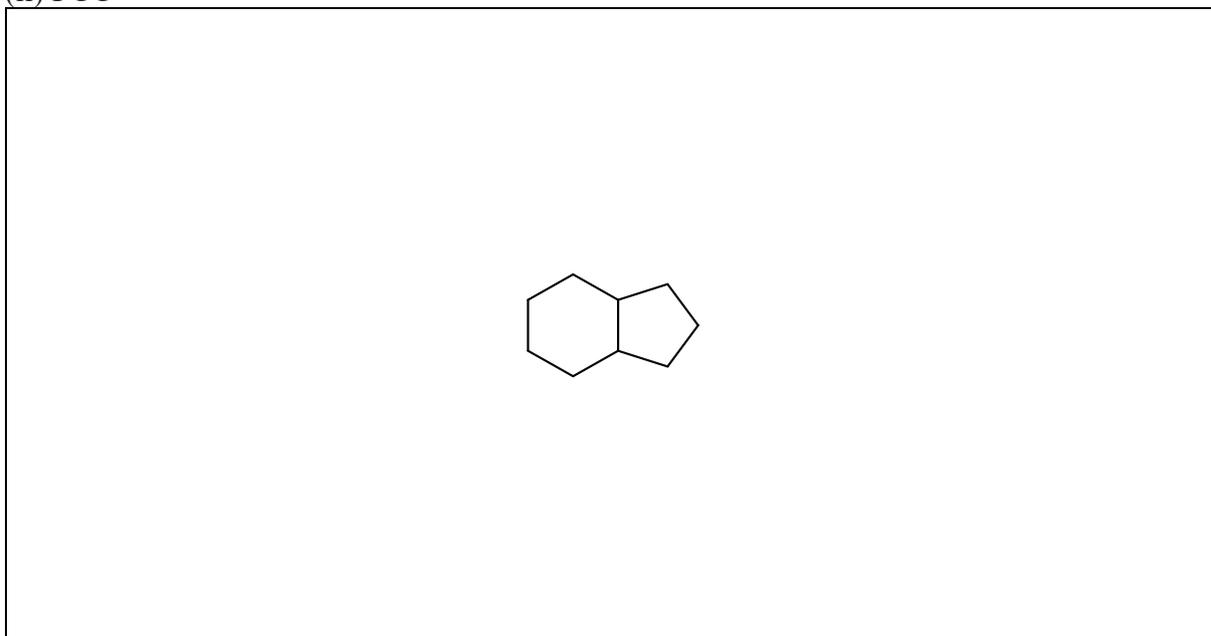


Draw the final product if C was first oxidized using each of the following reagents and then treated with DNPH. For simplicity, you can write DNPH on the sites where it reacts instead of drawing the complete structure of the product obtained. (A partial structure has been drawn for you.)

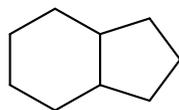
(i) Acidified KMnO₄



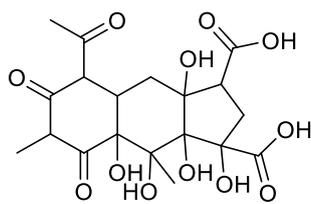
(ii) PCC



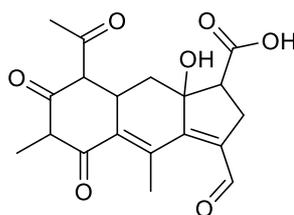
(iii) $I_2 / NaOH$



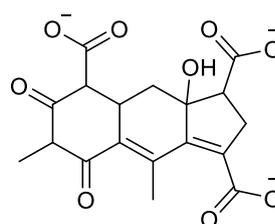
- e) An unknown compound D was treated with each of the above three reagents, giving the compounds shown below. Treatment with Tollens reagent showed no change, but a red precipitate was obtained with DNPH. Suggest the structure of the original compound D. (A partial structure has been drawn for you.)



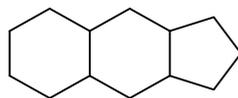
acidified $KMnO_4$



PCC



$I_2/NaOH$





Name :

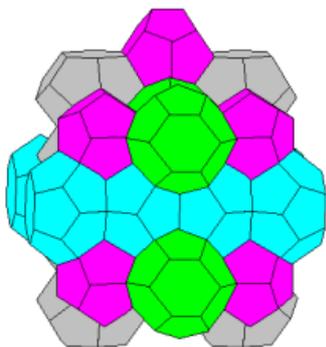
First name :

School :

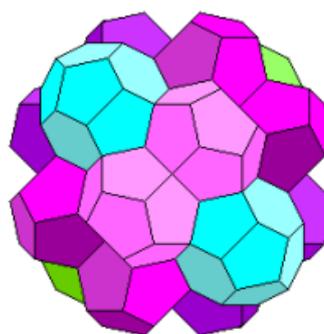
Problem III : Clathrates

3a	3b	3c	3d	3e	3f	3g	3h	3i	Total Problem III
2	4	3	3	3	3	3	2	2	25

Water can form a series of crystalline structures, called clathrates, which may contain small molecules. A common example is methane hydrate $(\text{CH}_4)_x(\text{H}_2\text{O})_y$ which can exist in two forms: the clathrate structures I and II.



Clathrate structure I



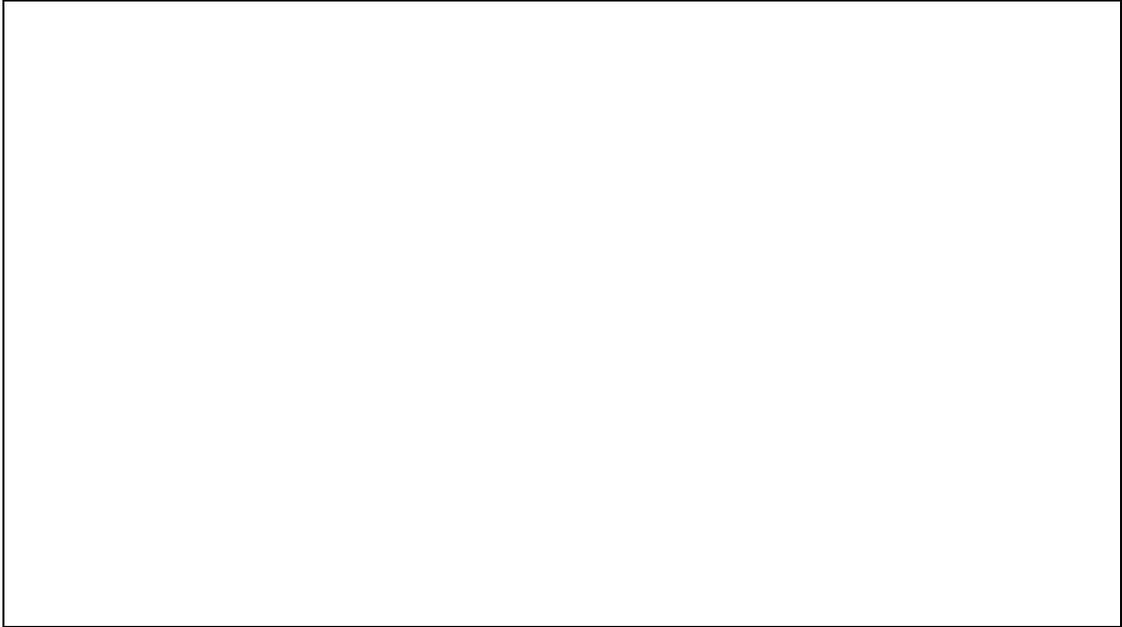
Clathrate structure II

Methane hydrates are a source of potential methane to meet our natural gas needs. Large reserves of methane hydrates have been found at the bottom of Lake Baikal, Russia.

- a) a) Write the balanced symbol equation for the combustion of methane in the presence of excess oxygen.

A sample of 100 g of methane hydrate, in the form of a clathrate of structure II $(\text{CH}_4)_x(\text{H}_2\text{O})_y$, is burned in a sealed container, in the presence of an excess of oxygen. After cooling the reaction products, 116.92 g of water are recovered in the chamber. In addition, the reaction of the produced gas with limewater (solution of $(\text{Ca}(\text{OH})_2)$, yields 84.73 g of CaCO_3 .

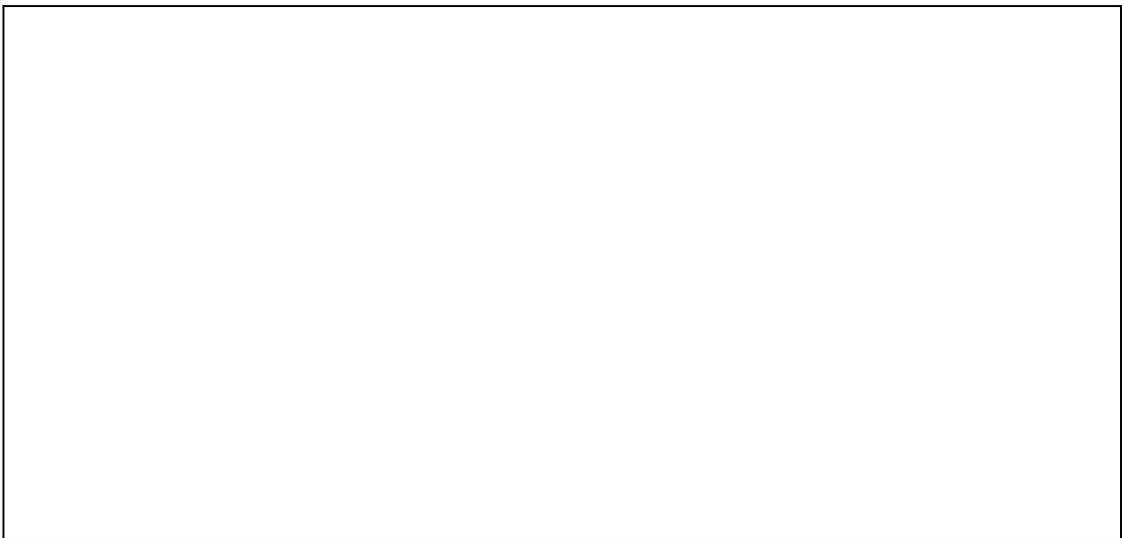
b) Determine the empirical formula of the methane hydrate shown as structure II.



c) The methane hydrate has a molecular mass of 2835,18 g/mol. Determine the molecular formula of Clathrate structure II.



d) On recent estimation, there are $6,67 \times 10^{11}$ kg of methane in Lake Baikal. Determine the volume of gas that is found in the lake during Winter at $-19,0$ °C with an atmospheric pressure of 1,0 bar.



The methane in lake Baikal can be found in the form of Clathrate structure I, whose formula is : $(\text{CH}_4)_8(\text{H}_2\text{O})_{46}$.

- e) Determine the percentage by mass of methane found in this hydrate.

- f) Using the information from questions d) and e), determine the total mass of methane hydrate that can be found in Lake Baikal.

- g) g) The density of the methane hydrate crystals is $0.95 \text{ g} \cdot \text{cm}^{-3}$. Calculate the volume of crystals at the bottom of Lake Baikal.

The elemental mesh is the smallest unit repeated within a crystal. The elemental mesh for methane hydrate structure I is a cube that contains 8 molecules of methane and 46 molecules of water.

- h) What is the mass of the elemental mesh ?

- i) Using the density of the methane hydrate (0.95 g cm^{-3}), calculate the length of the side of its elemental mesh.



Name :

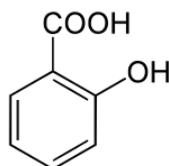
First name :

School :

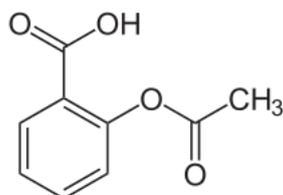
Probleme IV : Acetylsalicylic acid

4a	4b	4c1	4c2	4c3	4d	4e	4f1	4f2	Total Problem IV
2	2	2	4	3	2	4	5	3	27

This is a translation of an extract from a scientific article: *Famous for its antiseptic and analgesic properties, salicylic acid was also shown to be famous for the terrible heartburn it inflicted. Aspirin restricted this problem but did not suppress it: solid aspirin irritates the gastric mucosa. It was shown to be so important to avoid prolonged contact between acetylsalicylic acid and the mucosa that the laboratories have worked on various formulations of aspirin.* The semi-developed formula of salicylic acid, $C_7O_3H_6$, (molecular molar mass = $138.13 \text{ g} \cdot \text{mol}^{-1}$) is :



This is acetylsalicylic acid, $C_9O_4H_8$, (molecular molar mass = $180,17 \text{ g} \cdot \text{mol}^{-1}$) :



The solubility of acetylsalicylic acid in water is $3.4 \text{ g} \cdot \text{dm}^{-3}$ ($\text{g} \cdot \text{L}^{-1}$).

To simplify the writing, 'HA' will be used as the formula for acetylsalicylic acid.

A single aspirin tablet contains 500 mg of acetylsalicylic acid. It is stirred in a beaker with 50 cm^3 (mL) of water and the resulting solution ($V = 50 \text{ cm}^3$) has a pH of 2,6.

- a) Calculate the mass of acetylsalicylic acid that can actually be dissolved in 50 cm^3 (mL) of water.

- b) Is the tablet completely soluble in the glass of water? If not, calculate what remains in excess as a non-soluble mass.

- c) 1. Write the equation to show the reaction between acetylsalicylic acid (HA) and water:

2. From the pH measurement, calculate whether the reaction of HA with water is partial or complete.

3. Show, by calculation, that the pK_a value of acetylsalicylic acid matches that shown in the table of acidity constants and pK_a at the end of the problem.

To avoid some of the side effects of aspirin, less aggressive powders containing not solely acetylsalicylic acid but a mix of sodium acetylsalicylate and sodium bicarbonate (hydrogen carbonate) are sold. In France, one of these preparations is sold under the name *Catalgine*. In the concentrations used, sodium hydrogen carbonate (bicarbonate) and sodium acetylsalicylate (NaA) are completely soluble in water. When a sachet of *Catalgine* is labeled "*Catalgine* 0.50 g", this means that the active ingredient has been manufactured by the complete (quantitative) reaction of 0.50 g of acetylsalicylic acid with sodium hydroxide (NaOH).

d) Write the equation to show acetyl salicylic acid (HA) and sodium hydroxide (NaOH):

e) As a sachet of "0.50 g *Catalgine*" contains 0.80 g of a mixture of sodium acetylsalicylate and sodium hydrogen carbonate, calculate the amount of material and the mass of sodium acetylsalicylate (molar mass = 202,15 g mol⁻¹).

When dissolving a sachet of « *Catalgine* 0,50 g » in a beaker of de-ionised water, one obtains solution S, which has a pH of around 8.3.

f) 1. Show that in solution S, the active ingredient, namely acetylsalicylic acid, HA, is not a predominant molecule.

2. What are the 3 dominant molecules, excluding water ?

Acidity and pK_a constants of some conjugate acid-base pairs in aqueous solution at 298 K

<u>Couples</u>	K_a en (mol/L)	pK_a
HBr/Br ⁻	$\approx 1,0 \cdot 10^9$	≈ -9
H ₂ SO ₄ /HSO ₄ ⁻	$\approx 1,0 \cdot 10^9$	≈ -9
HClO ₄ /ClO ₄ ⁻	$\approx 1,0 \cdot 10^8$	≈ -8
HCl/Cl ⁻	$\approx 1,0 \cdot 10^7$	≈ -7
HClO ₃ /ClO ₃ ⁻	$\approx 5,0 \cdot 10^2$	$\approx -2,7$
H ₃ O ⁺ /H ₂ O	≈ 55	-1,74
HNO ₃ /NO ₃ ⁻	≈ 25	$\approx -1,4$
HIO ₃ /IO ₃ ⁻	$1,6 \cdot 10^{-1}$	0,8
H ₂ SO ₃ /HSO ₃ ⁻	$1,6 \cdot 10^{-2}$	1,8
HSO ₄ ⁻ /SO ₄ ²⁻	$1,0 \cdot 10^{-2}$	2,0
H ₃ PO ₄ /H ₂ PO ₄ ⁻	$7,6 \cdot 10^{-3}$	2,1
HF/F ⁻	$6,6 \cdot 10^{-4}$	3,2
HNO ₂ /NO ₂ ⁻	$6,3 \cdot 10^{-4}$	3,2
C ₉ O ₄ H ₈ /C ₉ O ₄ H ₇ (aspirine)	$3,2 \cdot 10^{-4}$	3,5
HCOOH/HCOO ⁻	$1,6 \cdot 10^{-4}$	3,8
CH ₃ COOH/CH ₃ COO ⁻	$1,8 \cdot 10^{-5}$	4,75
CO ₂ aq./HCO ₃ ⁻	$4,3 \cdot 10^{-7}$	6,4
H ₂ S/HS ⁻	$1,0 \cdot 10^{-7}$	7,0
H ₂ PO ₄ ⁻ /HPO ₄ ²⁻	$6,3 \cdot 10^{-8}$	7,2
HSO ₃ ⁻ /SO ₃ ²⁻	$6,3 \cdot 10^{-8}$	7,2
HClO/ClO ⁻	$3,2 \cdot 10^{-8}$	7,5
HBrO/BrO ⁻	$2,5 \cdot 10^{-9}$	8,6
HCN/CN ⁻	$6,0 \cdot 10^{-10}$	9,2
NH ₄ ⁺ /NH ₃	$5,7 \cdot 10^{-10}$	9,2
HCO ₃ ⁻ / CO ₃ ²⁻	$5,0 \cdot 10^{-11}$	10,3
HPO ₄ ²⁻ /PO ₄ ³⁻	$4,3 \cdot 10^{-13}$	12,4
HS ⁻ /S ²⁻	$1,2 \cdot 10^{-13}$	12,9
H ₂ O/OH ⁻	$1,8 \cdot 10^{-16}$	15,74
OH ⁻ / O ²⁻	$< \approx 1 \cdot 10^{-29}$	≈ 29
NH ₃ /NH ₂ ⁻	$< \approx 1 \cdot 10^{-35}$	≈ 35

Draft Sheet