CHIMIESOLYMPIAD
LËTZEBUERG 2021

SEMI-FINALS : Problems

Dear students,

We congratulate you for your participation in the Chemistry Olympiad and we wish you lots of success in this second round as well as in your studies and in all of your future endeavours. We also congratulate you for having succeeded in the first round, which has enabled you to tackle the "Problems" round today. **Before undertaking this next round, please carefully read the following instructions.**

Attached you will find 4 questions. The subjects of these questions are: general chemistry, stoichiometry, pH, redox and organic chemistry.

You have **two hours** to answer these questions. You can use a non-programmable calculator, but you cannot have any personal documents on you.

Include your name and your institution's name at the start of **each** question. Write your answers to each of the questions on the question paper (front and back, if necessary). **Clearly indicate your reasoning and your calculations. Justify your answers and indicate the units in the final answers.** The last page is a draft sheet which will not be taken into account for the final assessment. Detach the two first pages and keep them for reference.

Following the results of this second round, the 12 best students will be invited to participate in a final (practical) round, which will take place on **Saturday 24th April 2021 at the University of Luxembourg's Limpertsberg laboratories**. This final round will determine the 4 laureates of the national Chemistry Olympiad, and will also constitute the Luxembourg team for the 53rd IChO, which will be organized by Japan, from the 24th to July to the 2nd of August 2021. For more information, please see http://icho.olympiades.lu/.

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

Best wishes and good luck.
The Chemistry Olympiad organisers

Detach this sheet and keep it for information.

Useful Constants

(Detach this page if necessary)

LIÈGE université **TABLEAU PÉRIODIQUE DES ÉLÉMENTS**

masse atomique relative A_r — X élément — nombre atomique Z

1 I a	2 II a		3 III b	4 IVb	5 V b	6 VI b	7 VII b	8 VIII b	9 VIII b	10 VIII b	11 I b	12 II b	13 III a	14 IV a	15 V a	16 VI a	17 VII a	18 VIII a
1,01 H 1																		4,00 He 2
6,94 Li 3	9,01 Be 4												10,81 B 5	12,01 C 6	14,01 N 7	16,00 O 8	19,00 F 9	20,18 Ne 10
22,99 Na 11	24,31 Mg 12												26,98 Al 13	28,09 Si 14	30,97 P 15	32,07 S 16	35,45 Cl 17	39,95 Ar 18
39,10 K 19	40,08 Ca 20		44,96 Sc 21	47,88 Ti 22	50,94 V 23	52,00 Cr 24	54,94 Mn 25	55,85 Fe 26	58,93 Co 27	58,69 Ni 28	63,55 Cu 29	65,39 Zn 30	69,72 Ga 31	72,61 Ge 32	74,92 As 33	78,96 Se 34	79,90 Br 35	83,80 Kr 36
85,47 Rb 37	87,62 Sr 38		88,91 Y 39	91,22 Zr 40	92,91 Nb 41	95,94 Mo 42	Tc* 43	101,07 Ru 44	102,91 Rh 45	106,42 Pd 46	107,87 Ag 47	112,41 Cd 48	114,82 In 49	118,71 Sn 50	121,75 Sb 51	127,60 Te 52	126,90 I 53	131,29 Xe 54
132,91 Cs 55	137,33 Ba 56	(1) 57 - 70	174,97 Lu 71	178,49 Hf 72	180,95 Ta 73	183,9 W 74	186,21 Re 75	190,21 Os 76	192,22 Ir 77	195,08 Pt 78	196,97 Au 79	200,59 Hg 80	204,38 Tl 81	207,21 Pb 82	208,98 Bi 83	Po* 84	At* 85	Rn* 86
Fr* 87	Ra* 88	(2) 89 - 102	Lr* 103	Rf* 104	Db* 105	Sg* 106	Bh* 107	Hs* 108	Mt* 109	Ds* 110	Rg* 111	Cn* 112	Nh* 113	Fl* 114	Mc* 115	Lv* 116	Ts* 117	Og* 118

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

Constants

$R = 8{,}31\ \text{J·mol}^{-1}\text{·K}^{-1}$ $\quad 1F = 9{,}65 \cdot 10^{4}\ \text{C·mol}^{-1}$

$R = 8{,}21 \cdot 10^{-2}\ \text{L·atm·mol}^{-1}\text{·K}^{-1}$ $\quad N_A = 6{,}02 \cdot 10^{23}\ \text{mol}^{-1}$

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

Simplified pH formulas :

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

Buffer mix : $\text{pH} = \text{p}K_a + \log \frac{c_{base}}{c_{acid}}$

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

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Problem I : Test SARS-CoV2

1a	1b	1c	Total for problem I
4	6	4	14

Guanidinium thiocyanate ($C_2H_6N_4S$), also called GITC, is a reagent used to denature the proteins present in the SARS-CoV2 virus and allow the detection of its RNA by PCR (polymerase chain reaction). GITC can be obtained by 2 successive chemical reactions.

The first is to produce ammonium thiocyanate (NH_4SCN) by bubbling (the action of passing a gas through a liquid) gaseous carbon disulphide (CS_2) in an ammonia solution (NH_3 in aqueous solution). Then, the ammonium thiocyanate is isolated in solid form by evaporation of water. This is then converted to guanidinium thiocyanate by calcination at low temperature under an inert atmosphere. A characteristic odour due to the release of hydrogen sulphide gas is detectable during these 2 steps.

a) Write balanced symbol equation for these two reactions.

b) Knowing that the mass of the crucible containing the guanidinium thiocyanate after calcination is 32.2441g and that the mass of the empty crucible is 30.1763 g, assuming there is a complete reaction, calculate the concentration of the solution of ammonia used to produce ammonium thiocyanate, knowing that the volume of the starting aqueous solution is 100 mL.

Also calculate the minimum volume, in litres, of carbon disulphide necessary to bubble through this solution to produce NH_4SCN, at atmospheric pressure and at 25 ° C *c)* The ammonia solution is prepared by diluting a concentrated ammonia solution at 32% by mass of NH_3 (ρ = 880 kg·m^{-3}). Determine the volume of concentrated ammonia solution that must be used to prepare the 100 mL of diluted solution. *(If you could not determine the concentration of the dilute ammonia solution in point (b), assume it is 0.8 mol·L^{-1}.)*

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Problem II : Calcium carbide

2a	2b	2c	2d	2e	2f	Total for problem II
2	2	2	4	8	3	21

Calcium carbide CaC_2 is a greyish solid used in the production of ethyne. Calcium carbide is produced by the reaction of calcium oxide with carbon, forming calcium carbide and carbon monoxide.

a) Determine the balanced symbol equation for the formation of calcium carbide from calcium oxide.

b) Show the Lewis structure of the carbide ion C_2^{2-}.

German chemist Friedrich Wöhler (1800 - 1882) discovered that calcium carbide reacts with water, forming ethyne (C_2H_2) and calcium hydroxide. At the time, ethyne was burned in the lamps of miners and in the headlights of early motor vehicles.

c) Write the balanced symbol equation for the formation of ethyne from calcium carbide.

50 cm^3 (excess) of water is added to an impure sample of calcium carbide with a mass of 0.752 g. After all the calcium carbide has reacted, 20 cm^3 of the reaction mixture is taken and titrated with 0.25 $mol \cdot L^{-1}$ hydrochloric acid.

34.60 cm^3 is needed to neutralize the sample.

d) Assuming that none of the impurities in the sample reacted with hydrochloric acid, calculate the percentage mass of calcium carbide in the original sample.

0.833 g of the same sample is reacted with excess water. The ethyne formed from this reaction is burnt quantitatively in a combustion calorimeter ($c_K = 0.41\ kJ \cdot K^{-1}$), containing exactly 120 g of water (c of water = $4.19\ J \cdot g^{-1} \cdot K^{-1}$).

In calorimetry, the amount of energy transferred (Q) is given by the following equation:

$$Q = m \cdot c \cdot \Delta T$$

Q, the energy transferred
m, the mass of the material being heated or cooled
c, the specific heat capacity
ΔT, the change in temperature

e) Calculate the final temperature of the system, knowing that the calorimeter as well as the water had an initial temperature of 20.3 ° C. The enthalpy of combustion of ethyne is $\Delta_C H_m^0(C_2H_2) = -1255{,}6\ kJ \cdot mol^{-1}$.

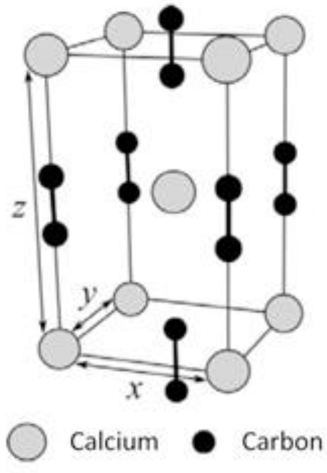
The diagram opposite represents the ionic lattice structure of calcium carbide. Calcium is positioned at the vertices and in the centre of the lattice.

In a lattice:

- the atoms located at the vertices of the lattice are found in 8 cells of the lattice (they count for 1/8);

- the atoms located on one face of the cell are common to 2 cells (they count for ½);

- the atoms located on the edges of the cell are common to 4 cells in the lattice (they count for ¼).



f) Considering the number of atom fractions contained in a cell within the lattice, indicate the number of calcium and carbon atoms contained in one cell within the lattice structure.

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School : ____________________________________

Problem III : Ammonia

3a	3b	3c	Total for problem III
2	10	5	17

The synthesis of ammonia by the Haber-Bosch process, which consists of the hydrogenation of atmospheric nitrogen gas in the presence of a catalyst, is of such importance that it consumes 1.4% of the world's energy annually.

a) Give the balanced symbol equation for the equilibrium synthesis of ammonia through the Haber-Bosch process.

Aquarium enthusiasts should also be concerned about the production of ammonia which, dissolved in aquarium water, is toxic to fish. Indeed, the denitrification of organic excretions produces ammonium ions which, at excessively high pHs, turn into ammonia.

b) A 100 litre aquarium has a pH of 8 and a total concentration of ammonia and ammonium ions of 1 mg/L. Calculate the concentration of ammonium ions assuming that there is no interaction with other substances and that ammonia is a weak base with a pK_b of 4.75.

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c) What mass of ammonium chloride should be added to a 500 mL solution of 0.2 M ammonia to obtain a buffer of pH = 9.0?

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Problem IV : Structure of organic compounds

4a	4b	4c	4d	4e	4f	4g	4h	4i	Total for problem IV
4	2	3	2	4	3	3	1	6	28

The empirical formula of a compound can be calculated from the relative proportions of the elements that make up that compound. Thus, it is possible to determine the empirical formula of an unknown organic compound from its elemental analysis.

Consider an unknown organic compound **C1** which contains only carbon, hydrogen and oxygen. Elemental analysis reveals the presence of 54.5% carbon and 9.15% hydrogen.

a) Determine the empirical formula of **C1**.

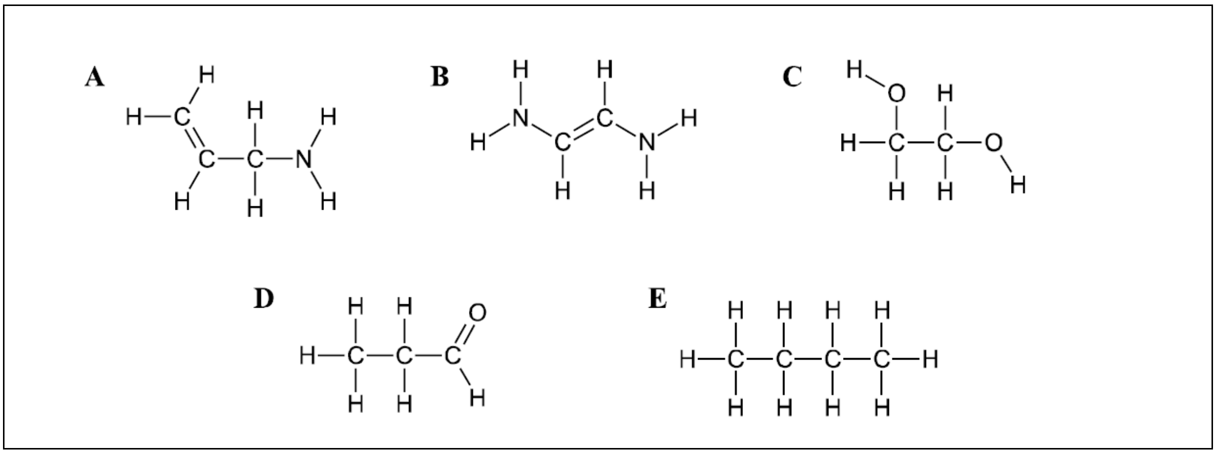
b) Deduce the molecular formula of **C1** if it has a molecular mass of 88 $g \cdot mol^{-1}$.

Mass spectrometry, which measures the mass-to-charge (m/z) ratio of molecules, is an important analytical technique in determining the structures of organic compounds. In a simplified version of mass spectrometry, the molecule to be analysed is ionized by removing an electron from it, to form a positively charged compound called the molecular ion.

We will assume for the remainder of this question that only mono-charged ions (charge z = 1) are detected and that therefore the m/z ratio is equal to the mass of the observed ion, m.

An unknown organic compound **C2** containing only carbon, hydrogen and oxygen is analysed by mass spectrometry.

c) Look at the following structures, circle those with a molecular mass of 58 $g \cdot mol^{-1}$.

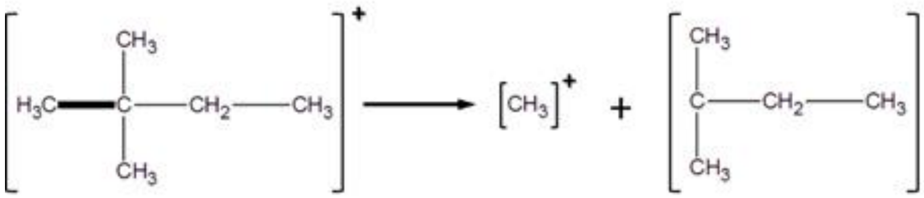


In order to determine which of these structures corresponds to true molecular structure of compound **C2**, the mass of the molecular ion of compound **C2** is determined more accurately (to more decimal places) by high-resolution mass spectrometry.

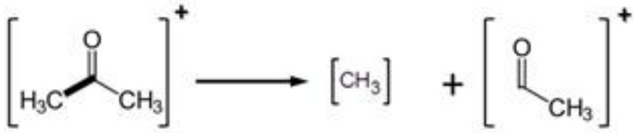
d) Considering the table below which shows the exact relative atomic masses of elements, identify the unique structure of compound **C2** if the ionic molecular mass is 58.0417 units.

Atom	**Relative atomic mass (u)**
^{12}C	12,0000
^{16}O	15,9949
^{1}H	1,0079
^{14}N	14,0031

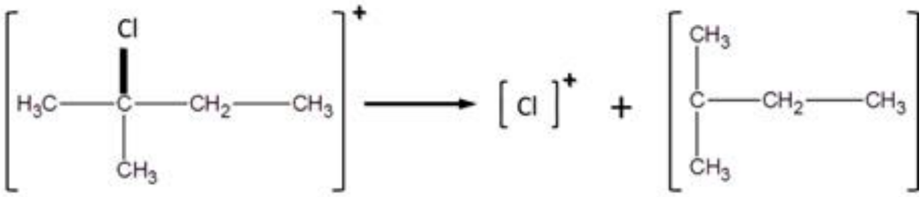
In mass spectrometry, if the molecular ion is unstable, it can fragment into smaller molecules (charged or not). Fragmentation of a molecular ion involves the breaking of bonds (usually the weakest in the molecule) and the formation of stable cationic fragments. It is generally predictable as shown in the figure below.



C - C bond at a ramification

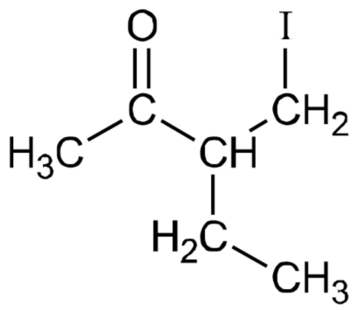


C - C bond next to a carbonyl group



C - X bond, where X is a heteroatom (O, N, S, Cl, I)

Compound **C3**, the semi-structural formula of which is given below, was analysed by mass spectrometry and several fragments were observed at m/z ratios of 15, 29, 43 and 127.



e) On the basis of the possible fragments (shown above), propose a structure (or semi-developed formula) for each of the fragments in the table below.

m/z=15	*m/z*=29	*m/z*=43	*m/z*=127

Another organic compound **C4** containing 4 carbon atoms and also containing hydrogen and oxygen is observed. Its molecular ion is characterized by an m/z ratio = 74.0729. In addition, other important fragments were observed at m/z = 15, 17 and 57.

f) Come up with a molecular formula for this compound using the table of exact relative atomic masses.

g) Propose a possible structure for the different fragments shown below.

m/z=15	*m/z*=17	*m/z*=57

h) Propose a semi-developed structural formula for the composition of **C4**.

Some elements exist in nature as a mixture of several isotopes in high natural abundance. Bromine has two abundant isotopes: ^{79}Br (49.3%) and ^{81}Br (50.7%). A compound containing a bromine atom will exhibit two peaks of molecular ions depending on which isotope it contains. One peak will correspond to the molecular ion containing ^{79}Br and the other will correspond to the molecular ion containing ^{81}Br. The two peaks will differ by two units of mass *m/z.*

The relative intensities of these two peaks will correspond to the relative abundance of each of the isotopes (49.3: 50.7). Chlorine and sulphur also exist in the form of several isotopes. These are presented in the table below:

Isotope	Natural abundance (%)
^{35}Cl	75,8
^{37}Cl	24,2
^{32}S	95,0
^{33}S	0,75
^{34}S	4,2

i) For each of the compounds below, determine the expected *m/z* values corresponding to the molecular ion and determine the relative intensity for each peak.

$CH_3CH_2CH_2$-SH

m/z	Relative intensity

Cl-$CH_2CH_2CH_2CH_2$-Cl

m/z	Relative intensity

Draft sheet