CHIMIESOLYMPIAD LËTZEBUERG 2024

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, acids and bases, reaction kinetics and chemical equilibrium.

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 school'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 considered 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, April 20th 2024**, **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 56th IChO, which will be organized by Saudi Arabia, from July 21st to July 30th 2024. For more information, please see https://chimie.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

Useful Constants

(Detach this page if necessary)

Periodic table of the elements

I																	**VIII**
1,0 H 1	**II**											**III**	**IV**	**V**	**VI**	**VII**	4,0 He 2
6,9 Li 3	9,0 Be 4											10,8 B 5	12,0 C 6	14,0 N 7	16,0 O 8	19,0 F 9	20,2 Ne 10
23,0 Na 11	24,3 Mg 12											27,0 Al 13	28,1 Si 14	31,0 P 15	32,1 S 16	35,5 Cl 17	39,9 Ar 18
39,1 K 19	40,1 Ca 20	45,0 Sc 21	47,9 Ti 22	50,9 V 23	52,0 Cr 24	54,9 Mn 25	55,8 Fe 26	58,9 Co 27	58,7 Ni 28	63,5 Cu 29	65,4 Zn 30	69,7 Ga 31	72,6 Ge 32	74,9 As 33	79,0 Se 34	79,9 Br 35	83,8 Kr 36
85,5 Rb 37	87,6 Sr 38	88,9 Y 39	91,2 Zr 40	92,9 Nb 41	95,9 Mo 42	(97) Tc 43	101,1 Ru 44	102,9 Rh 45	106,4 Pd 46	107,9 Ag 47	112,4 Cd 48	114,8 In 49	118,7 Sn 50	121,8 Sb 51	127,6 Te 52	126,9 I 53	131,3 Xe 54
132,9 Cs 55	137,3 Ba 56	57-71	178,5 Hf 72	180,9 Ta 73	183,8 W 74	186,2 Re 75	190,2 Os 76	192,2 Ir 77	195,1 Pt 78	197,0 Au 79	200,6 Hg 80	204,4 Tl 81	207,2 Pb 82	209,0 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
223 Fr 87	226 Ra 88	89-103	(267) Rf 104	(268) Db 105	(269) Sg 106	(270) Bh 107	(269) Hs 108	(278) Mt 109	(281) Ds 110	(282) Rg 111	(285) Cn 112	(286) Nh 113	(289) Fl 114	(290) Mc 115	(293) Lv 116	(294) Ts 117	(294) Og 118

Lanthanides	138,9 La 57	140,1 Ce 58	140,9 Pr 59	144,2 Nd 60	(145) Pm 61	150,4 Sm 62	152,0 Eu 63	157,3 Gd 64	158,9 Tb 65	162,5 Dy 66	164,9 Ho 67	167,3 Er 68	168,9 Tm 69	173,0 Yb 70	175,0 Lu 71
Actinides	(227) Ac 89	232,0 Th 90	231,0 Pa 91	238,0 U 92	(237) Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(266) Lr 103

Constants

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

$R = 8,21 \cdot 10^{-2} \text{ L·atm·mol}^{-1}\text{·K}^{-1}$ $\qquad$ $N_A = 6,022 \cdot 10^{23} \text{ mol}^{-1}$

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: $pH = pK_a + \log\frac{c_{base}}{c_{acid}}$ $\qquad$ at 25 °C : $K_w = K_{H_2O} = [H_3O^+]\cdot[OH^-] = 1,0\cdot10^{-14}$

Thermochemistry:

|	
$\Delta_R H = Q_p + W$	$\Delta_R G = \Delta_R H - T \cdot \Delta_R S$
$\Delta_R S = \dfrac{Q}{T}$	$\Delta_R G = -R \cdot T \cdot \ln K$

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NAME : _____

First name : _____

School : _____

Problème I: All around cheese

1	2	3	4	5	6	7	8	9	10	11	Total Problem I
2	1	1	2	2	2	2	2	4	6	6	30

Although there are many differences in the cheese-making process, the transformation of lactose into lactic acid during fermentation is a key chemical process, whatever the origin of the cheese.
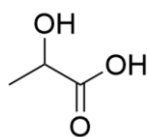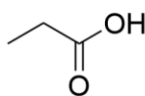
lactic acid   propanoic acid

The dissociation constant of lactic acid is $K_a = 1{,}38 \cdot 10^{-4}$ mol/L.

1. Write down the formula and systematic name (IUPAC) of the conjugate base of lactic acid.

2. Calculate the pK_a of lactic acid.

Lactic acid is a stronger acid than propanoic acid. This is due to a hydrogen bridge that stabilises its conjugate base.

3. Draw the structure of the conjugate base of lactic acid showing this hydrogen bridge.

The lactose initially contained in milk is a disaccharide with the formula $C_{12}H_{22}O_{11}$. During the first stage of its transformation into lactic acid, lactose is converted into two monosaccharides, **A** and **B**.
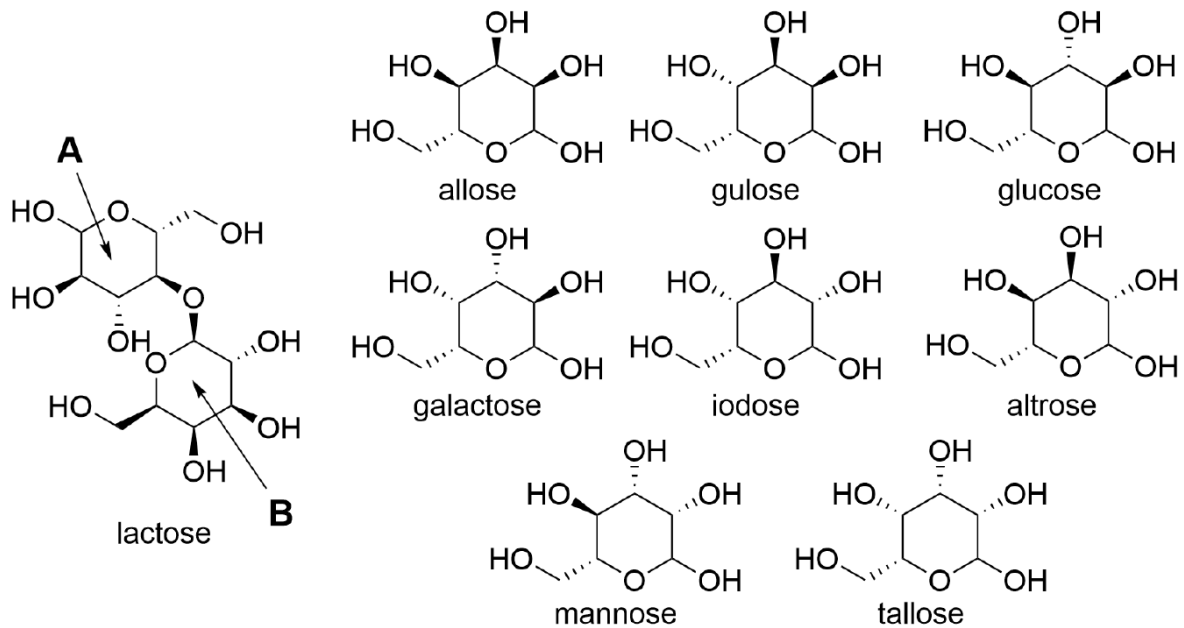
4. How can we classify the reaction of lactose to form the two monosaccharides? Tick the correct answer.

	Oxidation
	Reduction
	Condensation
	Hydrolysis
	Isomerisation
	Elimination

5. Write down the names of the monosaccharides (**A** and **B**) that make up lactose.

The conversion of lactose into lactic acid is carried out by bacteria as part of a complex biochemical process, but lactic acid is often the only product.

6. Write an equation (using molecular formulae) for the conversion of lactose into lactic acid.

Many varieties of Swiss cheese, such as Emmental, are famous for the holes or 'eyes' that appear in the cheese. To produce these holes, another species of bacteria, Propionibacterium freudenreichii, plays an important role. This bacterium transforms lactic acid into propanoic acid, ethanoic acid, carbon dioxide and water. The production of carbon dioxide causes the bubbles to appear.

7. Write an equation (using molecular formulae) for the production of carbon dioxide by this bacterium. In the balanced reaction, lactic acid is the only reactant, and ethanoic acid and carbon dioxide are produced in equal quantities.

Let's assume that during fermentation at 21°C, a spherical bubble 1.5 cm in diameter appears in the cheese.

8. Calculate the volume of this bubble in m^3.

9. Assuming that the bubble consists of pure CO_2 at atmospheric pressure, p_{atm} = 101 325 Pa, calculate the mass of lactic acid that was fermented by the bacteria to produce the bubble. For the calculation, assume that CO_2 obeys the law of ideal gases.

Note: the abbreviation for "dissolved in cheese" is (ch).

Carbon dioxide dissolved in cheese can exist in two forms: dissolved carbon dioxide gas, $CO_{2(ch)}$, or dissolved hydrogen carbonate, $HCO_{3(ch)}^-$. The following equilibrium is established between these two chemical species:

$$CO_{2(ch)} + 2\ H_2O \rightleftharpoons HCO_{3(ch)}^- + H_3O_{(ch)}^+$$
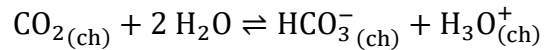
with
$$K = \frac{\left[H_3O_{(aq)}^+\right]\left[HCO_{3(ch)}^-\right]}{\left[CO_{2(ch)}\right]} = 4,47 \cdot 10^{-7}\ \text{mol/L}$$

where [X] designates the concentration of X at equilibrium.

At the end of fermentation, we find that $\left[CO_{2(ch)}\right] + \left[HCO_{3(ch)}^-\right] = 3,70 \cdot 10^{-2}$ mol/L and pH = 5.20.

10. Calculate the equilibrium concentration of carbon dioxide dissolved in the cheese, $[CO_{2(ch)}]$.

We will now examine how CO_2 bubbles (the "eyes") of a certain size form during the first stages of fermentation. Suppose a bubble of radius r is in contact with a fixed volume of cheese V_{ch} at temperature T. The pressure of the CO_2 inside the bubble, p_b, is related to the concentration of dissolved CO_2 by Henry's law,

$$\left[CO_{2(ch)}\right] = k_H \cdot p_b$$
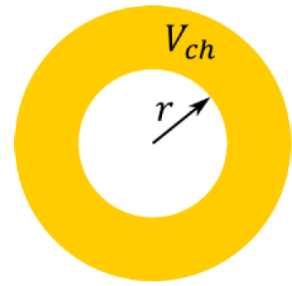
with k_H = Henry's law constant for the solute CO_2 and the solvent "cheese".

11. In the table below, tick the expression that calculates the quantity of matter of $CO_{2(g)}$, $CO_{2(ch)}$ and $HCO_{3(ch)}^-$ as a function of p_b, r, k_H, V_{ch}, T and the pH.

Suppose that $CO_{2(g)}$ obeys the law of ideal gases under these conditions.

	$k_H \cdot V_{ch} \cdot p_B$	$\dfrac{4\pi r^3 p_b}{3RT}$	$\dfrac{4\pi r^3 p_b}{3RT} \cdot K \cdot 10^{pH}$	$K \cdot 10^{pH} \cdot k_H \cdot V_{ch} \cdot p_b$	$\dfrac{V_{ch} p_b}{3RT}$	$K \cdot 10^{-pH} \cdot k_H \cdot V_{ch} \cdot p_b$
$n_{CO_{2(g)}}$						
$n_{CO_{2(ch)}}$						
$n_{HCO_3^-(ch)}$						

Problem II: The chemistry of the atmosphere

1	2	3	4	5	6	7 (i)	7 (ii)	7 (iii)	Total Problem II
2	2	3	2	3	3	2	2	2	21

A radical is a species with a free (unpaired) electron on the outer layer. It is obtained by radiation or heating. This breaks a bond homolytically: one electron is found in each of the two new species, creating two free radicals.

Studying the reactions that take place in the atmosphere is crucial to understanding the global climate and minimising the impact of human activity on the environment. Hydrogen sulphide H_2S is a molecule with an interesting chemistry in the atmosphere. H_2S is present in natural gas and is also particularly present near volcanoes.

The main process by which H_2S is naturally eliminated from the air is its reaction with the $OH\cdot$ radical (the main oxidising agent in the atmosphere). The reaction occurs in a single shock between H_2S and the $OH\cdot$ radical.

1. Give an equation for the reaction of H_2S with the $OH\cdot$ radical to form water and another radical.

To determine the rate constant of the reaction, H_2S was generated in the laboratory by reacting iron (II) sulphide with hydrochloric acid.

2. Give an equation for the generation of H_2S in the laboratory.

The average emission rate of H_2S into the air of a volcanic region can be estimated at $7.65 \cdot 10^5$ molecules cm^{-3} s^{-1}.

However, the concentration of H_2S has been measured to be constant over time, which means that the rate at which H_2S is produced is the same as the rate at which H_2S is consumed in that volcanic region.

For a reaction that occurs between two species A and B, the speed of the reaction is given by:

$$\text{reaction speed} = k \cdot [A] \cdot [B]$$

where k is the corresponding rate constant, and [A] and [B] are the concentrations of A and B respectively.
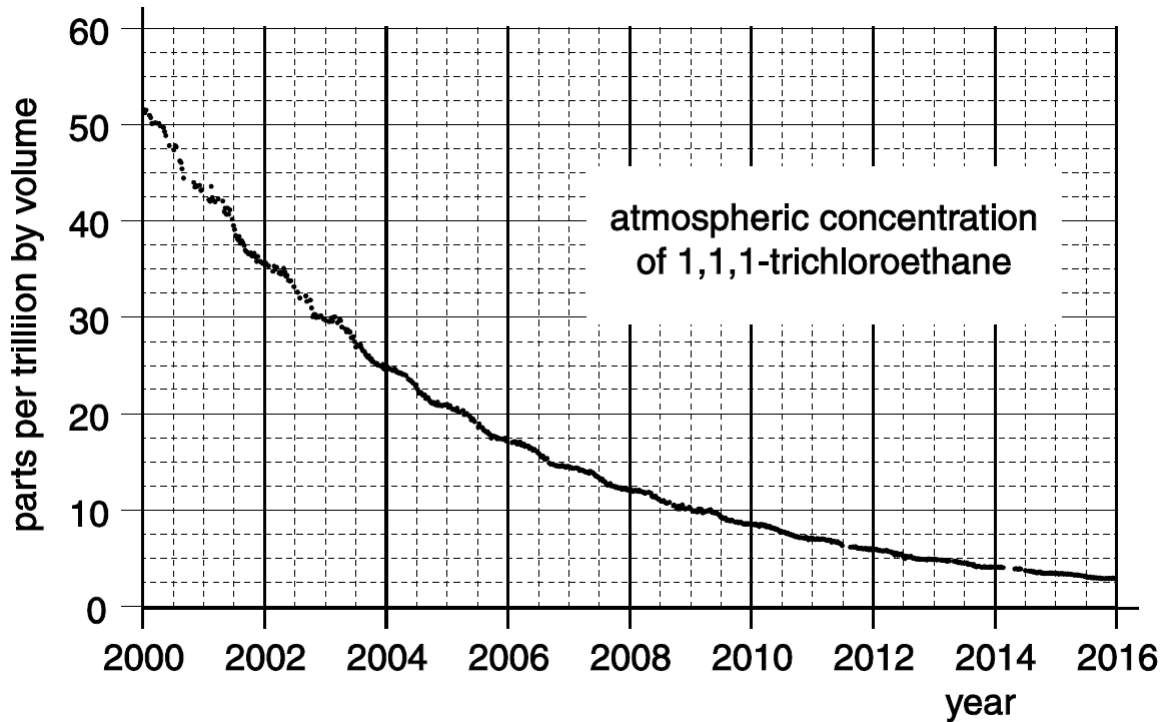
3. Calculate the concentration of H_2S in the atmosphere in the unit $\text{molecules} \cdot \text{cm}^{-3}$. Assume that the only process for removing H_2S from the atmosphere is its reaction with the OH· radical, and that the average concentration of the OH· radical is $1.1 \cdot 10^6 \ \text{molecules} \cdot \text{cm}^{-3}$. The rate constant for the H_2S consumption reaction (question 1) has been measured as $k = 4.7 \cdot 10^{-12} \ \text{cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$.

4. The average concentration of H_2S is usually expressed in $\mu g \cdot m^{-3}$. Express the H_2S concentration found in part (3) in $\mu g \cdot m^{-3}$.

It is very difficult to measure the concentration of OH· radicals directly, so we often have to resort to indirect methods. As well as H_2S, the OH· radical is capable of oxidising other compounds in the atmosphere, such as 1,1,1-trichloroethane. Since atmospheric emissions of 1,1,1-trichloroethane ceased in the 1990s, its change in concentration can be used indirectly to estimate the average global concentration of the OH· radical. The concentration profile of 1,1,1-trichloroethane over time shows a simple exponential decrease, typical of reactions following first-order kinetics.

5. Using the graph below, estimate the half-life ($t_{1/2}$) of 1,1,1-trichloroethane. Give your answer in seconds, assuming that 1 year = 365.25 days.

Assuming that the concentration of OH· radicals is constant over time and that the only process for removing 1,1,1-trichloroethane from the atmosphere is its reaction with OH·, the apparent rate constant (k_{app}) of the reaction can be found using the following expression :

$$t_{1/2} = \frac{\ln 2}{k_{app}}$$

The apparent rate constant, k_{app}, is a product of the second-order rate constant ($k_{2nd} = 1{,}0 \cdot 10^{-14} cm^3 \cdot molecules^{-1} \cdot s^{-1}$) and the concentration of OH· radicals.

Explanation: If the concentration of a chemical species is kept constant, it can be combined with the rate coefficient and the rate law can be simplified (pseudo-first-order reaction).

6. Using your value for the half-life of 1,1,1-trichloroethane, calculate the average total atmospheric concentration of OH· radicals in the unit molecules · cm^{-3}.

(Note: you may not get exactly the same result as the concentration given in the first part of the problem).

Natural gas often contains sulphur in the form of H_2S. To minimise sulphur emissions from natural gas desulphurisation, the H_2S is partially burnt to form SO_2, which then reacts with the remaining H_2S to form elemental sulphur.

7.(i) Give an equation for the combustion of H_2S.

(ii) Give the reaction equation between H_2S and SO_2.

(iii) Show that reaction (ii) is a mediamutation reaction.

Problem III : Renewable fuels

1	2	3	4	5	6	7	8	9	Total Problem III
1	3	3	4	3	1	2	4	8	29

Given the limited availability of fossil fuels, scientists are constantly looking for renewable and, if possible, more environmentally friendly alternatives. For this reason, interest in hydrogen as an energy carrier or for the use of biofuels has begun to grow. Hydrogen is likely to play a major role in the decarbonisation of our society, as its reaction with dioxygen easily 'releases' large quantities of energy, while forming water as its only product.

Switching to hydrogen as an energy carrier would also go some way to solving the problem of climate change, just as the electrolysis of water powered by photovoltaic panels would make it possible to produce hydrogen without CO_2 emissions or the use of fossil fuels. Unfortunately, we're not there yet.

At present, almost all the hydrogen available in the world does not come from the electrolysis of water, but is still of fossil origin. Unlike the hydrogen produced by water splitting (known as green hydrogen), this hydrogen (known as grey hydrogen) not only requires methane, currently mainly of fossil origin, but also generates carbon monoxide as a by-product during its synthesis. The process for synthesising grey hydrogen is called steam reforming, and the associated chemical reaction is as follows:

$$CH_4 + H_2O \leftrightharpoons CO + 3\,H_2$$
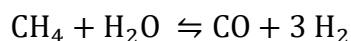
This equilibrium reaction is characterised by an equilibrium constant K_p. When all the components of the equilibrium reaction are gaseous, the equilibrium constant K_p is preferred to the equilibrium constant K_c. Both constants can be calculated in the same way from the law of mass action. The only difference is that to calculate the value of K_p, we use the partial pressures $p_{(i)}$ of the different components instead of their concentrations $c_{(i)}$.

T [K]	K_p [atm^2]
780	0,0132
820	0,0702
860	0,3218
900	1,2946
940	4,4618
980	15,0374
1020	44,5253
1060	121,6893
1100	309,5796
1140	738,4565

1. For this steam reforming reaction, write down the expression for the equilibrium constant K_p.

2. During a synthesis test in the context of a pilot project, 3 kg of methane are reacted with 3 kg of water. What is the maximum mass of hydrogen that can be produced, assuming that the reaction is not limited to equilibrium ?

3. Consider a 50 L synthesis vessel heated to a temperature of 1140 K. For the 3 kg of each reactant injected, determine their partial pressure (in atm), assuming that methane and water can be considered as ideal gases.

4. From 3 kg of each reactant, at a time t, the partial pressure of CO is 40 atm at 1140 K. According to the equilibrium constants K_p for the steam-forming reaction given in the table above, is the reaction at equilibrium at this time t ? Justify your answer!

5. As the quantity of hydrogen that can be produced by steam reforming is much less than the quantity of dihydrogen that could theoretically be produced from the quantities of reactants used in the absence of equilibrium, we are constantly looking for ways to make this reaction more economic. What are two methods of increasing the yield of this reaction? Is one of the methods suggested more economical than the other?

One of the characteristics of an efficient fuel is the amount of energy it releases during combustion, i.e. its enthalpy of combustion. Hydrogen, for example, has a combustion enthalpy of around -286 kJ/mol. One method of determining the enthalpy of combustion is to use the average binding enthalpies. Some average bond enthalpies are given below.

bond	Average binding enthalpy ($kJ \cdot mol^{-1}$)
$C - C$	347
$C - H$	413
$O = O$	498
$C - O$	358
$C = O$	805
$O - H$	464

6. Draw up the skeletal formula for 2,2,4-trimethylpentane, one of the main isomers found in petrol.

7. Write down the equation (using molecular formulae) for the complete combustion of 2,2,4-trimethylpentane.

8. Calculate the enthalpy of combustion of 2,2,4-trimethylpentane using the average binding enthalpies given in the table above.

In order to reduce the consumption of non-renewable resources, a start has been made on adding 5 or 10 percent of ethanol produced from renewable resources to fuels. This is indicated by the values E5 and E10 on petrol pumps. Let's assume that one litre of E5 fuel contains 50 mL of ethanol and 950 mL of 2,2,4-trimethylpentane. The density of pure ethanol is $0.789 \text{ g} \cdot \text{cm}^{-3}$ and the density of the octane isomer is $0.703 \text{ g} \cdot \text{cm}^{-3}$. Let's also assume that there is no change in volume during mixing.

9. Different compositions of fuels containing only ethanol and 2,2,4-trimethylpentane have been analysed in terms of the amount of energy they emit. Determine the composition of the mixture that emits 30.05 MJ, when one litre of this mixture is burned. The compositions are not limited to the two E5 and E10 blends currently on sale at service stations.

   The enthalpy of combustion of ethanol using average binding enthalpies is $-1276 \text{ kJ} \cdot \text{mol}^{-1}$. If you have not found the value for the enthalpy of combustion of 2,2,4-trimethylpentane in (8), use $-4800 \text{ kJ} \cdot \text{mol}^{-1}$.

Problem IV: Unknown salts

A	B	Total Problem IV
10	10	20

Part A

The elemental analysis of a salt **A** of metal **X** that can be purchased provides the following data:

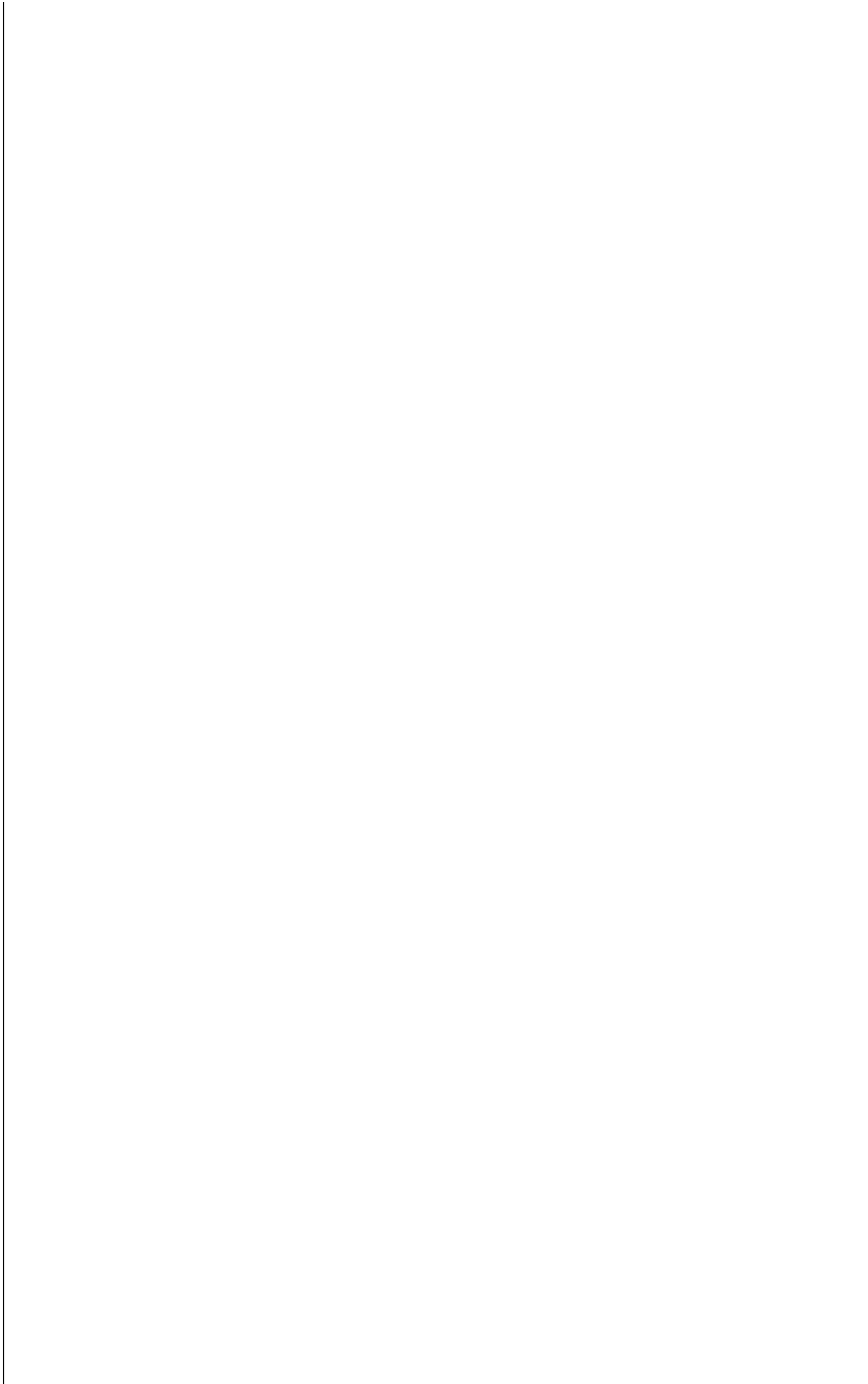| Element	Percentage by mass
Carbon	0,00
Hydrogen	3,62
Oxygen	57,38
Nitrogen	0,00
Chlorine	0,00
Sulfur	14,38

A unit of formula **A** contains only one atom **X** and no elements other than those indicated in the elemental analysis. If **A** is analysed by thermogravimetry (a physico-chemical analysis that studies the gain or loss of mass of a substance when heated or cooled continuously as a function of temperature or time), a total loss of mass of around 32% of the initial mass is detectable until complete decomposition.

The aqueous solution of **A** shows, among other things, the following reaction:

$$A \xrightarrow[\text{BaCl}_2]{\text{dilute HCl}} \text{white precipitate}$$

Determine the metal **X**, give the molecular formula of the compound and identify the salt **A**.

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Part B

A 2.000 g sample of a double hydrated salt **B**, containing two different metal ions, of formula $M_Y(M_Z)_2(SO_4)_4 \cdot 22\ H_2O$, is heated strongly to remove all the water, leaving a residue of 1.1103 g. Identify the salt **B**, knowing that M_Y is an ion of one the following elements: Ca, Ti, Fe or Ba.

Draft Sheet