CHIMIESOLYMPIAD
LËTZEBUERG 2023

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, 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 **training day**, which will be organised on April 1st, 2023, **at the University of Luxembourg's (Limpertsberg) laboratories**. Furthermore, these 12 students will also be allowed to participate in a final, practical round, which will take place on **Saturday, April 29th 2023.** This final round will determine the 4 laureates of the national Chemistry Olympiad, and will also constitute the Luxembourg team for the 55th IChO, which will be organized by Switzerland, from July 16th to July 25th 2023. 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

Detach this sheet and keep it for information.

LE GOUVERNEMENT DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Éducation nationale, de l'Enfance et de la Jeunesse
ACLg
UNIVERSITÉ DU LUXEMBOURG
Fonds National de la Recherche Luxembourg
CHAMBRE DE COMMERCE LUXEMBOURG
CHAMBRE DES SALARIES LUXEMBOURG
andré losch fondatioun

Useful Constants

(Detach this page if necessary)

relative atomic mass atomic number	A_r X Z	element

1 I a	2 II a		3 III b	4 IVb	5 V b	6 VI b	7 VII b	8 VIII b	9	10	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

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

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

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

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: $\mathrm{pH} = \mathrm{pK_a} + \log\frac{c_{base}}{c_{acid}}$ $\quad$ at 25 °C : $K_w = K_{H_2O} = [H_3O^+]\cdot[OH^-] = 1{,}0\cdot 10^{-14}$

Thermochemistry:

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

NAME : ______________________________

First name : ___________________________

Lycée : ______________________________

Problem I : Carbon dioxide

1a	1b	1c	1d	1e	1f	1g	1h	Total Problem I
3	2	2	2	3	2	3	7	24

Carbon dioxide is an important ingredient in the food and beverage industries. During the summer of 2018, there was a shortage of CO_2, which resulted in supermarkets limiting the delivery of refrigerated goods, and it affected the production of beer. This is a somewhat ironic situation, given the well-documented increase in atmospheric CO_2 levels.

a) Draw the Lewis structures of CO and CO_2.

b) Determine the different oxidation numbers of carbon in carbon dioxide and carbon monoxide.

The English chemist William Henry studied the equilibria of gases dissolved in liquids. He proposed that the concentration of the dissolved gas (in a liquid) is proportional to the partial pressure of the gas (in the gas phase above the liquid). This factor of proportionality is known as Henry's constant. For CO_2 Henry's constant has a value of $3{,}3 \cdot 10^{-2}\ \mathrm{mol} \cdot \mathrm{dm}^{-3} \cdot \mathrm{atm}^{-1}$. Sealed drinks containers contain dissolved CO_2 that is in equilibrium with a small amount of gaseous CO_2 above the solution.

c) The partial pressure of gaseous CO_2 in a fizzy drink can of 250 cm^3 is 3,0 atm at 25 °C. What is the concentration of CO_2 in the solution?

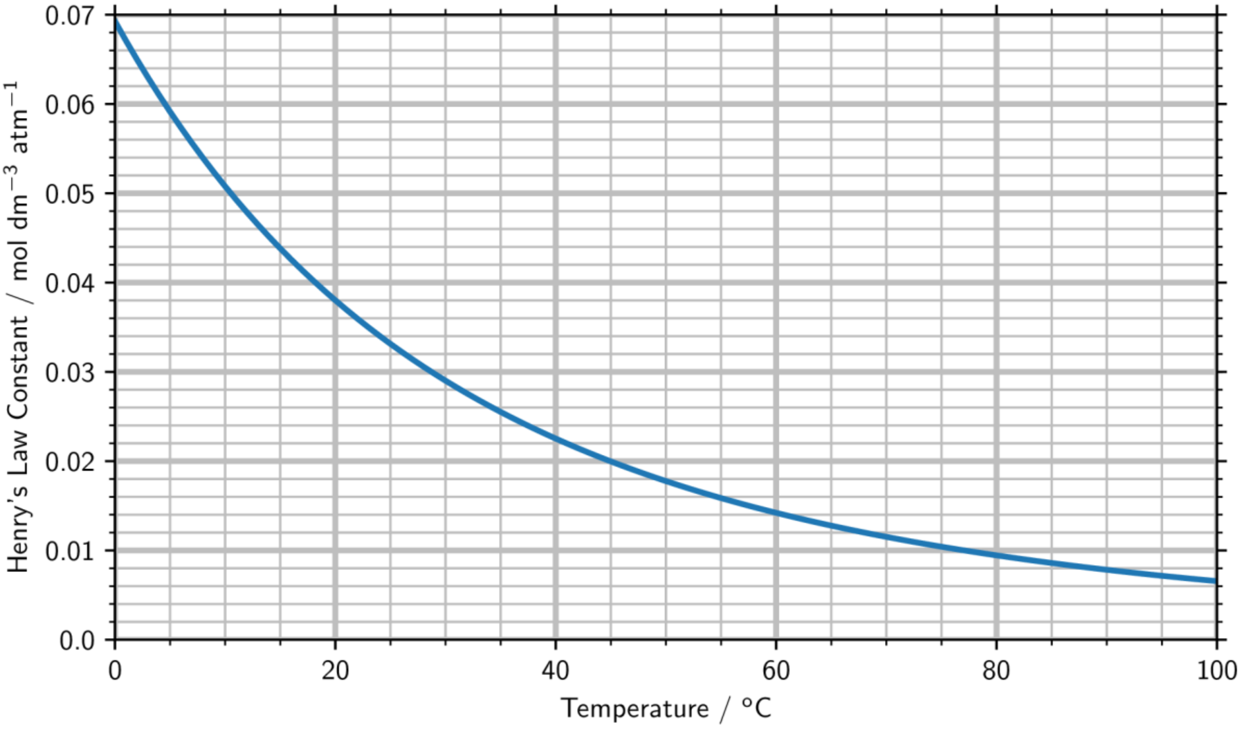
d) What mass of CO_2 is dissolved in the solution (in the can of 250 cm^3)?

e) Let's assume that the can only contained CO_2 as a gas and no solution. Calculate the pressure in the can at 25 °C, using the mass of CO_2 that was calculated in part (d).

f) In what conditions would CO_2 gas be most soluble in water ?
Tick the box with the correct option:

☐ high pressure and low temperature
☐ high pressure and high temperature
☐ low pressure and low temperature
☐ low pressure and high temperature

g) The maximum pressure that a fizzy drink can is able to withstand, is 7 atm. Using the graph below, determine the maximum temperature at which the container can be stored safely.



One of the methods to produce CO_2 in industry is the Haber-Bosch process.

Step 1: $CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$
Step 2: $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$
Step 3: $CO + H_2O \rightleftharpoons CO_2 + H_2$

Ammonia (produced in step 2) is largely used to produce fertilizer. Fertilizer production is often stopped during summer. Coupled with the increased demand of fizzy drinks in the hot summer of 2018, the production stop of fertilizer contributed to a shortage of CO_2. In step 3, an initial mixture of 40 moles of CO, 20 moles of H_2 and 20 moles of CO_2 in contact with 40 moles of water vapor reached an equilibrium at 1100 K. At 1100 K, this reaction has a K_p of 0,64.

h) Calculate the number of moles of each gas leaving the reactor after having reached equilibrium.

NOM : ____________________________________

Prénom : __________________________________

Lycée : ___________________________________

Problem II : Precious metals and alloys

2a	2b	2c	2d	2e	Total Problem II
3	3	10	2	3	21

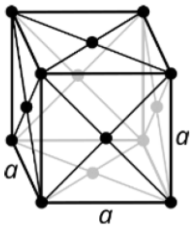
Gold, silver, copper and roentgenium are metals of group 11 in the periodic table; neutral atoms of these elements have a closed-shell d electronic configuration.

a) Indicate the electronic configurations of gold, silver and copper.
Note: Electronic shells that are completely filled, can be designated with the configuration of the respective noble gas.

The heavier species, roentgenium, was produced for the first time in Darmstadt in 1994. In the particle accelerator, bismuth (Bi is composed of a single isotope) was bombarded with atoms of another element. The nuclear fusion process produces atoms of roentgenium-272, as well as the same number of neutrons.

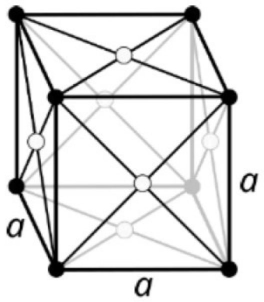
b) Establish the equation for the nuclear reaction using the atomic number and mass.

In standard conditions, all three metals form a face-centred cubic crystal structure (shown herewith), which has a high density.



	Atomic radius (pm)	**a (pm)**	ρ **(kg · m^{-3})**
Gold	144	407	19400
Silver	145	409	10490
Copper	128	362	8960

Because their atomic radii are very similar, gold and silver can be mixed in any ratio in an alloy; their relative spatial distributions then depend on the statistics. Gold and copper can also be mixed in any ratio, producing among others the ordered superstructure $AuCu_3$, shown herewith.



c) Calculate the density of the superstructure $AuCu_3$ assuming a direct contact of the atoms (as far as this is possible).
Note that the diagonal of the cube surface $d_f = \sqrt{2} \cdot a$

The copper content in a bronze or brass sample can be determined via electrogravimetry. A brass sample of 1,857 g (< 2 g) was first dissolved in concentrated nitric acid, then diluted in water to yield a final sample solution of 200,0 mL.

d) Explain why the first step must be done in a fume hood.

For the electrogravimetric determination, a 20,0 mL aliquot of the sample solution is subjected to electrolysis. A platinum electrode is used as the cathode; during electrolysis its mass steadily increases from 9,8354 g to 9,9266 g and then stays constant.

e) Calculate the copper content of the sample.

NOM : ______________________________

Prénom : ______________________________

Lycée : ______________________________

Problem III : *Curiosity*

3a	3b	3c	3d	3e	3f	3g	3h	Total Problem III
2	6	4	2	7	2	1	3	27

The landing of the Curiosity rover on Mars in August 2012 was realized with the aid of propulsion agents based on hydrazine. Hydrazine, N_2H_4, is very appreciated by NASA as it produces no carbon dioxide.

When hydrazine is passed over a catalyst it decomposes into a hot gaseous mixture that gives rise to thrust. During the decomposition, ammonia can be formed as an intermediary.

a) Write the balanced equation for the decomposition reaction of hydrazine into ammonia and dinitrogen.

Hydrazine can be produced by reacting ammonia with hydrogen peroxide:

$$2\ \mathrm{NH_3(g)} + \mathrm{H_2O_2(l)} \rightarrow \mathrm{N_2H_4(l)} + 2\ \mathrm{H_2O(l)} \quad |\ \Delta_r H^\circ = -241{,}0\ \mathrm{kJ}$$

b) Determine the enthalpy for the decomposition reaction of hydrazine based on the standard formation enthalpies:

$\Delta_f H^\circ(\mathrm{NH_3}) = -46{,}1\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta_f H^\circ(\mathrm{H_2O_2}) = -187{,}8\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta_f H^\circ(\mathrm{H_2O}) = -285{,}8\ \mathrm{kJ \cdot mol^{-1}}$

The Messerschmitt Me 163 was the first jet propulsion fighter plane. It was operated by reacting « C-Stoff » (a mixture of hydrazine with methanol) with « T-Stoff » (hydrogen peroxide).

Hydrogen peroxide reacts with hydrazine according to the following equation:

$$N_2H_4(l) + 2\ H_2O_2(l) \rightarrow N_2(g) + 4\ H_2O\ (l)$$

c) Determine the oxidation numbers of nitrogen and oxygen in each of the reactants and products.

d) Hydrogen peroxide oxidizes methanol into carbon dioxide and water. Write the balanced equation for this reaction.

e) A fighter jet can carry 225 litres of hydrazine and 862 litres of methanol. Calculate the thermal energy that is generated (under standard conditions) for the combustion of this quantity of fuel; use the standard enthalpy and density values hereafter. Assume that hydrazine and methanol are completely burnt.

$\Delta_C H°(N_2H_4) = -622{,}2\ \mathrm{kJ \cdot mol^{-1}}$ $\rho(N_2H_4) = 1{,}021\ \mathrm{g \cdot cm^{-3}}$

$\Delta_C H°(CH_3OH) = -726{,}0\ \mathrm{kJ \cdot mol^{-1}}$ $\rho(CH_3OH) = 0{,}7918\ \mathrm{g \cdot cm^{-3}}$

In rocket fuels, hydrazine is often mixed with dinitrogen tetroxide, N_2O_4, to form a hypergolic propellant, where the propellants spontaneously ignite when they come into contact with each other. NASA has already used N_2H_4 / N_2O_4 in various space vehicles and it may one day be implemented in cars.

f) The reactions in rockets give rise to more stable chemical products (∴ exothermic reactions) in the gaseous state (∴ to provide thrust). Identify the products for the reaction of N_2H_4 with N_2O_4.

g) Heating pure N_2O_4 leads to formation of a brown gas. What is the chemical formula of this gas?

A hydrazine derivative with the formula $C_2H_8N_2$ was used as a rocket propellant in the Apollo missions. Its structure contains two nitrogen atoms that are in different chemical environments, while the two carbon atoms are in identical chemical environments.

h) Draw the structure of $C_2H_8N_2$.

NOM : ________________________________

Prénom : ______________________________

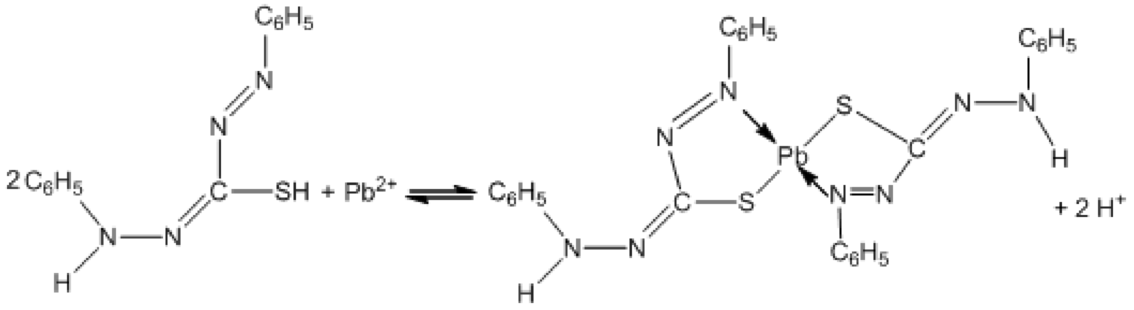
Lycée : ________________________________

Problem IV : Forensic Laboratory

4a	4b	4c	4d	Total Problem IV
14	5	5	4	28

The crime-scene investigation team is investigating the death of a man who was found at home in his armchair. A glass filled with water was recovered from the crime scene; forensic analysis of its contents revealed a presence of lead nitrate. In order to investigate the nature of the death (natural or poisoning), a blood probe of the deceased was sent to laboratory for analysis.

As blood is a complex mixture, lead must be extracted via a liquid-liquid extraction method. Dithizone is an organic molecule, which in the deprotonated form (called dithizonate) forms a red-orange complex with lead (see Figure). Dithizone and the complexes of dithizonates are soluble in organic solvents.



Complexation reaction of lead with dithizone

To carry out a liquid-liquid extraction, dithizone is dissolved in 25 mL of chloroform and the solution is added to a separating funnel. 15 mL of blood is diluted to 250 mL in a volumetric flask to produce solution S1. Then 10 mL of solution S1 are transferred to the separating funnel, before 25 mL of ammonia buffer are also added to the separating funnel to deprotonate the dithizone. The contents of the separating funnel are vigorously shaken, before letting the phases separate for 2 min. The organic phase is recovered from the separating funnel into a volumetric flask of 100 mL, topping up the volume with chloroform, to yield solution S2.

To quantify the lead in the solution, one makes use of the absorbance, noted **A**; absorbance is the capacity of a solution to absorb light at a particular wavelength. **A** depends on 3 parameters: the extinction coefficient (ε_λ, intrinsic parameter of a substance at a particular wavelength), the length of light path through the solution (d in cm) and the concentration of the substance in solution (c in mol·L^{-1}).

$$A = \varepsilon_\lambda \cdot d \cdot c$$

In order to obtain the unknown concentration in the blood sample solution S2, variable volumes of a standard solution of known concentration are added to a fixed volume of S2. By plotting absorbance as a function of the concentration of the standard solution, a straight-line fit can be obtained. The x-axis intercept then allows the unknown concentration of the sample solution (S2) to be determined; note that the intercept value will be negative.

The lead standard solution is prepared by reacting lead metal with 6M nitric acid. When the lead has fully dissolved, the obtained solution is diluted with distilled water and the extraction of the lead with a chloroform solution of dithizone is carried out according to the same method as the sample. The organic phase is then recovered in an S3 volumetric flask, topped up with chloroform.

Solutions S4 – S8 are prepared according to the volumes indicated in Table 1. Then, the absorbance measurements are carried out on those 5 solutions. Figure 1 displays the results from those measurements as a graph.

	S2	**S3**	**$CHCl_3$**
S4	10 mL	0 mL	15 mL
S5	10 mL	4 mL	11 mL
S6	10 mL	6 mL	9 mL
S7	10 mL	8 mL	7 mL
S8	10 mL	10 mL	5 mL

Tab.1 : Compositions of solutions S4 – S8

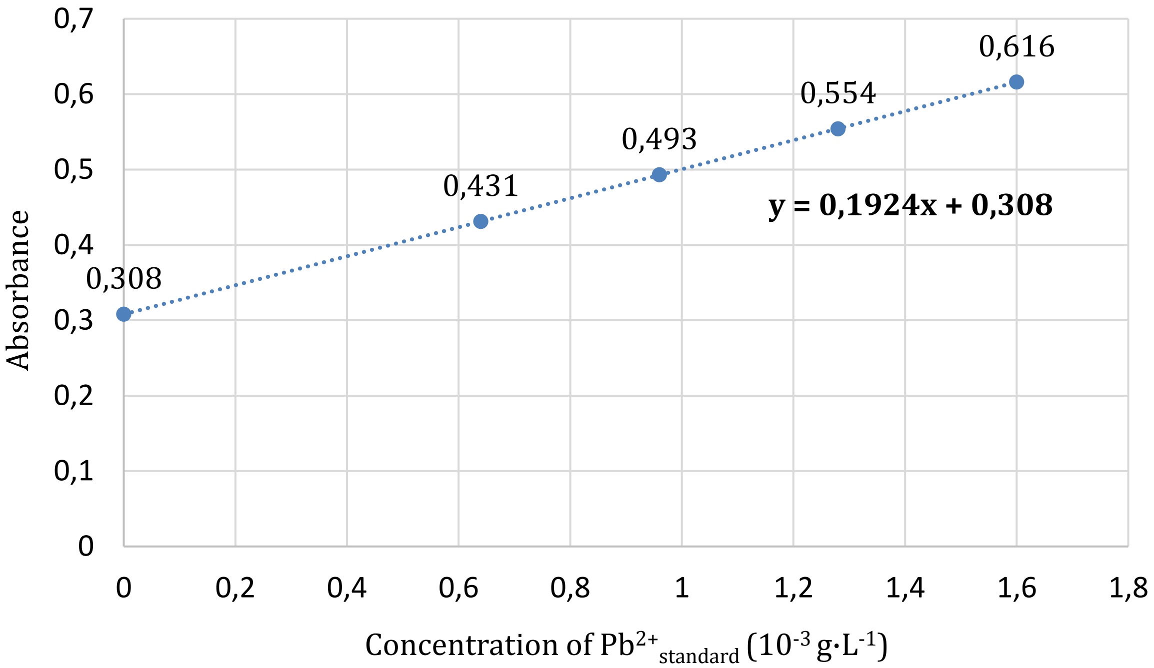


Fig.1. Absorbance as a function of the lead concentration

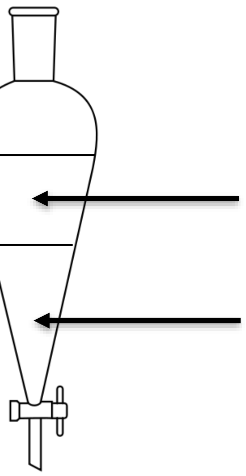
a) Let's assume that the deceased weighed 75 kg, that a human body contains on average 5 L of blood, and that the lethal concentration of blood nitrate is 93 mg/kg. Determine if the deceased was poisoned or if the death had natural causes. Show your detailed calculations leading to your conclusion.

b) Assuming that the length of the light path was 1 cm, calculate the extinction coefficient (ε) of the lead-dithizone complex.

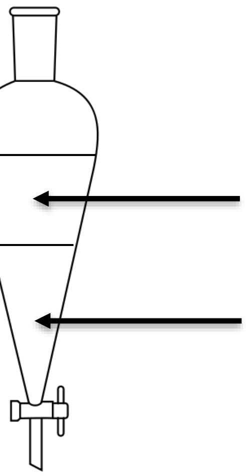
c) The 6 M nitric acid solution utilized to react with lead was prepared from a concentrated nitric acid solution of 70% by mass (ρ = 1,4 g·cm^{-3}). Calculate the required volumes of the 70% by mass solution and of water to prepare 100 mL of the 6 M solution.

d) Indicate the following items next to the separating funnel (see arrows): the aqueous phase, the organic phase, chloroform (ρ = 1,49 kg/L), lead (Pb^{2+}), dithizone and dithizonate, both before and after the addition of the ammonia buffer solution.

Before the addition of the ammonia buffer



After the addition of the ammonia buffer



Scrap paper