Question 1. Phosgene was used during the World War I as a poisonous gas. It can be prepared by the action of sunlight on a mixture of carbon monoxide and chlorine gases. Phosgene has the following elemental composition by weight: 12.14% C, 16.17% O and 71.69% chlorine. Its molecular weight is 98.9 g mol^{-1}.

(a) Determine the molecular formula of this compound;

(b) Using the average binding enthalpy, estimate the ΔH for formation of gaseous phosgene from CO(g) and $Cl_2(g)$.

Data:

$\Delta H°_{C-O}$ = 358 kJ mol^{-1}, $\Delta H°_{C=O}$ = 799 kJ mol^{-1}, $\Delta H°_{C\equiv O}$ = 1072 kJ mol^{-1}

$\Delta H°_{Cl-Cl}$ = 242 kJ mol^{-1}; $\Delta H°_{C-Cl}$ = 328 kJ mol^{-1}

Question 2. In a Styrofoam calorimeter it was placed 75.0 g of water at an initial temperature of 25.00°C. A mass of 1.60 g of NH_4NO_3 was added to the same recipient at the same temperature. After dissolution of the salt the final temperature was 23.34 °C. Consider that the specific heat capacity of the solution is 4.18 J $°C^{-1}g^{-1}$ and no energy was lost by the system:

(a) Explain if the dissolution reaction of this salt is exothermic or endothermic.

(b) Compute the variation of enthalpy for the dissolution of NH_4NO_3 in J mol^{-1}

Question 3. A student of chemistry was studying in a lab when he saw a colorless solution. He would like to know what the solution was, but there were no labels. This luck guy has found three solutions: A) NaCl, B) KNO_3 and C) NaOH. So, using his knowledge in general chemistry he put solution A, B and C in three test tubes with the "unknown solution" and observed:

Solution A + unknown solution: It was observed a white precipitate

Solution B + unknown solution: Nothing occurs

Solution C + unknown solution:It was observed a dark precipitate

Based on his observations the student was in doubt about the composition of unknown solution and proposed some hypotheses: i) $BaCl_2$; ii) $AgNO_3$ or iii) KBr.

(a) What is the composition of “unknown solution”?

(b) Write all three reactions above used to identify them.

Question 4. Answer the following questions:

(a) The half-cell A is formed by a bar of cadmium dipped in a solution of Cd^{2+} (1 $molL^{-1}$) and the half-cell B is formed by a bar of copper dipped in a solution of Cu^{2+} (1 $molL^{-1}$). Both were connected, one by one, with a half-cell of standard hydrogen electrode and the values recorded were:

Half-cell A: $Cd^{2+} + 2\ e^- = Cd$ $\quad \varepsilon^0 = -0.40$ V

Half-cell B: $Cu^{2+} + 2\ e^- = Cu$ $\quad \varepsilon^0 = +0.34$ V

Consider half-cell A and B, draw an electrochemical cell with spontaneous reaction (write the global equation) and calculate the cell potential. Furthermore, you need to indicate: the flow of electrons, cathode and anode.

(b) Metallic copper (Cu^0) can be dissolved by $HNO_{3(conc)}$ and it is observed the release of $NO_{(g)}$ which is oxidized to $NO_{2(g)}$. Considering this information, answer the question: Why metallic copper is solubilized by concentrated nitric acid and not by concentrated hydrochloric acid*?*

Data:

$2\ H^+ + 2\ e^- = H_2$ $\quad \varepsilon^0 = 0.00$ V

$Cu^{2+} + 2\ e^- = Cu$ $\quad \varepsilon^0 = +0.34$ V

$NO_3^- + 4H^+ + 3\ e^- = NO + 2\ H_2O$ $\quad \varepsilon^0 = +0.96$ V

$Cl_2 + 2\ e^- = 2\ Cl^-$ $\quad \varepsilon^0 = +1.36$ V

Question 5. In a lecture on covalent bonds, a student, making associations between H and Li in terms of number of electrons on the valence shell, asks the teacher if it is possible the existence of a molecule Li_2, as the molecule H_2 exists.

(a) Using your understanding on chemical bond, show if it is possible the existence of the molecule Li_2.

(b) Describe an experiment by which you could verify if such a molecule can exist or not.

Question 6.

(a) The dissociation energies for HF, HCl, HBr and HI are 543, 419, 354 and 287 kJ mol^{-1}, respectively. Explain the decreasing of the dissociation energy for these acids as the atomic number of the halogen increases.

(b) Consider the diatomic molecules N_2, O_2, and F_2. Order the molecules according to their dissociation energies. Justify your answer.

Question 7. Given a chemical reaction of the type:

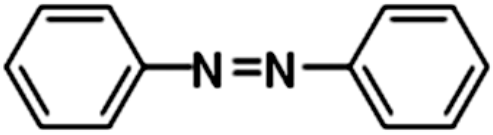
$$R = 2P$$

the forward reaction presents activation energy of E_a = 2 kJ mol^{-1} and rate constant of k_a = 0.01 s^{-1}. The backward reaction presents activation energy of E_b = 4 kJ mol^{-1} and rate constant of k_b = 0.01 L $mol^{-1}s^{-1}$.

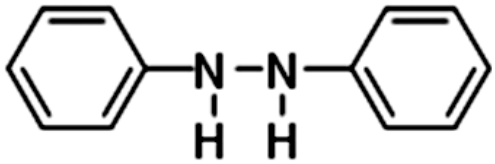
(a) What should be the direction of spontaneous reaction?

(b) What should be the rate law for the forward reaction and what the rate law of the backward reaction?

Question 8. Azo compounds are organic dyes used among other applications as textiles colorant. Many of them derive from azobenzene ($C_{12}H_{10}N_2$).



Azobenzeno



Hidrazobenzeno

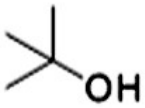
(a) Which is the hybridization of the nitrogen atom in each of the compounds below?
(b) Azobenzene is known to have greater delocalization of its π electrons than the hydrazobenzene. Provide an explanation for this statement based on non-hybridized atomic orbitals and N-N-C bond angles in each of these molecules.

Question 9. The molecule of ethyl butanoate ($C_6H_{12}O_2$) is responsible for the smell of pineapple.

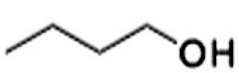
(a) Determine the mass of carbonic gas and water produced in the complete combustion of 1 mg of ethyl butanoate.

(b) What is the volume of O_2 at the **STP** conditions necessary to produce the complete combustion of 1 mg of ethyl butanoate?

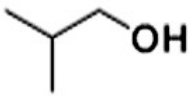
Question 10. Consider the following saturated alcohols (p.f. = Fusion Point; p.e. = Boiling Point):



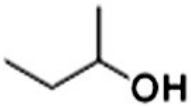
tert-butanol
p.f. 25 °C
p.e. 82 °C



butanol
p.f. -89 °C
p.e. 118 °C



isobutanol
p.f. -102 °C
p.e. 108 °C



sec-butanol
p.f. -115 °C
p.e. 99 °C

(a) Establish a relationship between the structure and the boiling point in the series.

(b) Put these compounds in ascending order of nucleophilicity.

Question 11. The following table contains some properties of some chemical elements:

Element	Atomic number	Atomic radius (pm)	Ionization energy ($kJ.mol^{-1}$)
K	19	227	418,8
Na	11	186	495,8
Ga	31	122	578,8
Ca	20	197	589,8

(a) Explain the crescent order of ionization energy observed in the table showing the effects involved.

(b) The following table contains the melting point for some compounds formed by some of the elements in the above table:

Compound	Melting point (°C)
CaF_2	1418
NaF	993
KF	858

How do you explain these differences among the melting points?

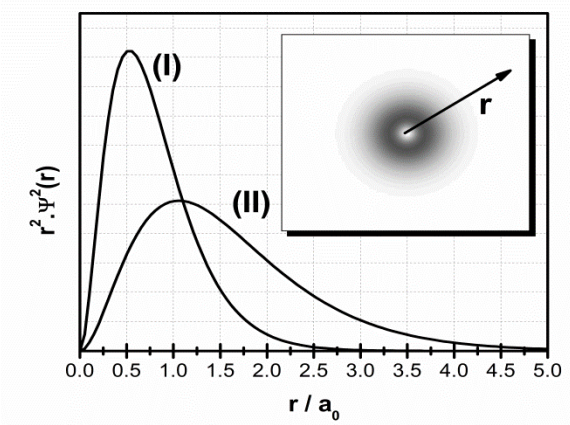
Question 12. Replacing H atoms by Cl atoms in acetic acid cause changes in acidity.

(a) Explain the trend observed in the acidity of the series reported below.

Acid	Ka (25 °C)
CH_3COOH	1.8×10^{-5}
$CH_2ClCOOH$	1.4×10^{-3}
$CHCl_2COOH$	3.3×10^{-2}
Cl_3CCOOH	2.0×10^{-1}

(b) Calculate the pH of a 0.01 mol L^{-1} solution for the strongest and for the weakest acid.

Question 13. The following figure presents the radial distribution functions for the 1s orbitals for two one-electron systems (I and II). (a_0 = 52,9 pm)



(a) Which of these systems (I or II) has the highest ionization energy? Justify your answer.

(b) The atoms in the figure correspond to H and He^+. Which curve in the figure describes the He^+ 1s orbital? Justify your answer.

Question 14. Answer the following questions:

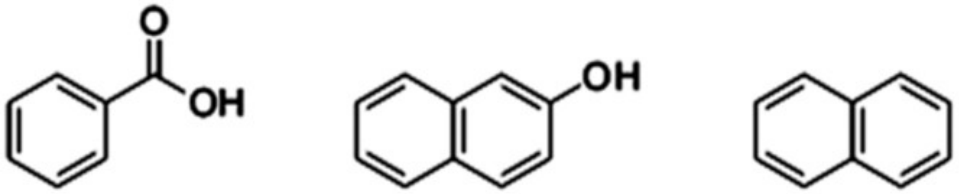
(a) According to the table below, it is possible to find values of K_{sp} for silver halides. What could explain the differences of solubility in water for the compounds?

Silver halides	**K_{sp}**
AgF	Soluble in water
AgCl	1×10^{-10}
AgBr	5×10^{-13}
AgI	2×10^{-16}

(b) Lattice energy (ΔH_{latt}) of a solid can not be measured directly. Therefore, is necessary using a thermodynamic cycle, as Born-Haber cycle. This cycle presents a correlation between lattice energy and thermodynamic parameters. Based on Born-Haber cycle, calculate the lattice energy to $NaCl_{(solid)}$ and write the complete cycle.

Data: $\Delta H_{formaton}$: -411 kJ mol^{-1}; $\Delta H_{vaporazation\text{-}Na}$: 108 kJ mol^{-1}; $\Delta H_{bond:Cl\text{-}Cl}$: 242 kJ mol^{-1}; $\Delta H_{ionization\text{-}Na}$: 502 kJ mol^{-1}; $\Delta H_{\text{electron affinity: Cl}}$: -354 kJ mol^{-1}.

Question 15. Consider that you have a mixture composed of equimolar amounts of β-naftol, benzoic acid and naphthalene in diethyl ether.



(a) Suggest a method for their separation from the mixture considering that you have in the laboratory an aqueous $NaHCO_3$ solution and an aqueous NaOH solution. For clarity, make a flow diagram.
(b) Justify the proposed method and give the reactions.

Question 16. The boiling point of ethers is similar to the boiling point of alkanes of same molecular weight (FW), but differs significantly in relation to the alcohols having similar FW. Comparing their solubility in water, ethers and alcohols of similar FW present comparable solubilities, whereas alkanes of similar molecular weight are insoluble. Consider the data in the table below.

	Compound	FW	Solubility g/100 mL of water
A	$CH_3CH_2OCH_2CH_3$	74	7,5
B	$CH_3[CH_2]_3CH_3$	72	insoluble
C	$CH_3[CH_2]_2CH_2OH$	74	9

(a) Explain why compounds (1) and (3) have similar solubilities in water, and why compound (2) is insoluble in this solvent.
(b) Among these compounds, which one should present the higher boiling point? Justify your answer.

Tabela Periódica e seus Elementos

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	ununnium 111 Uuu [272]	unubium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]