QUESTION 1

A) The force constants (k) for the homonuclear molecules C_2, N_2 and F_2 are very different from each other, being determined (not necessarily in this order) as 2260 $N.m^{-1}$, 930 $N.m^{-1}$ and 450 $N.m^{-1}$. Justifying your answer, assign these force constants to the molecules C_2, N_2 and F_2.

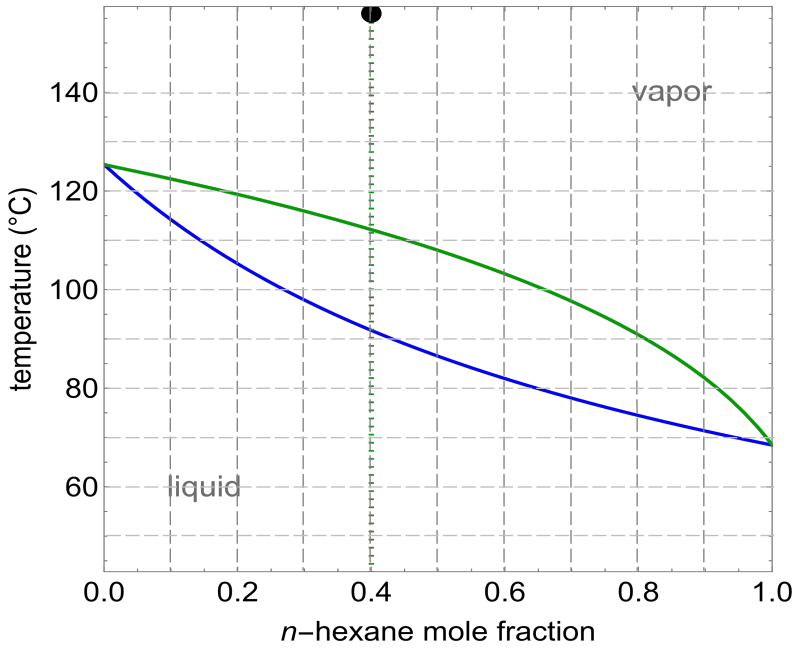
B) From the Lewis structures and using the valence shell electron repulsion model, the following statements were made:

I. The PCl_3F_2 molecule has a trigonal bipyramidal shape.
II. SnF_4 is a square planar molecule.
III. IF_5 has a pair of non-bonding electrons and a square pyramidal structure, with angles of approximately 90° and 180°.
IV. The PCl_3 molecule is non-polar due to its trigonal geometry.
V. The XeO_4^{4-} ion has an octahedral geometry, while the neutral XeO_4 molecule has a tetrahedral form, being all the Xe-O bonds of the same length.

Which alternative has the correct statements?

a) I, II
b) II, III, IV
c) III, IV
d) I, II, III
e) I, III, V

QUESTION 2



Analyzing the phase diagram of a n-hexane/n-octane mixture at 1 bar, 3 statements are made:

I. There is the formation of an azeotropic mixture

II. A decrease in pressure would shift the curves downwards towards lower temperature

III. The boiling temperature of the mixture with a molar fraction of 0.5 boils at the average of the boiling temperatures of the pure liquids.

The statements that are correct are:

a) I
b) II
c) III
d) I e II
e) II e III

B) Answer the following questions regarding a fractional distillation of the mixture with a molar fraction of n-hexane of 0.4:

a) At what temperature does this mixture come to boiling?

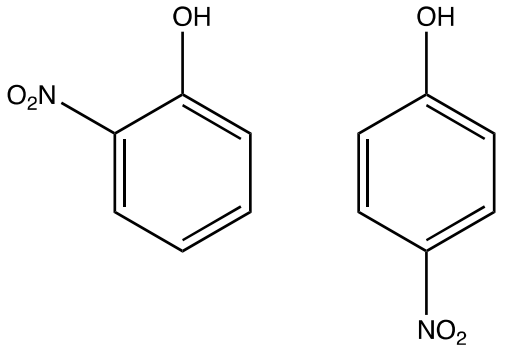
b) What is the percentage of n-hexane in the composition of the vapor formed?

c) What is the condensing temperature of this vapor?

d) If the condensate from the previous item is evaporated again, what will be the new percentage of n-hexane in this mixture?

QUESTION 3

A) Nitrophenol (M = 139,110 g mol^{-1}) is extremely important because its isomers are precursors to the drug paracetamol and mesalazine. It is synthesized by direct nitration of phenol with $NaNO_3/H_2SO_4$ through electrophilic aromatic substitution (EArS). This reaction yields two constitutional isomers with large melting point difference. The figure below shows these two isomers and their melting points.



o-nitrophenol *p*-nitrophenol

M.P. = 46 °C M.P. = 114 °C

Consider the following affirmatives about the melting point difference:

I – *o*-Nitrophenol has the lower melting point due to a strong intramolecular interaction; hydrogen bond between nitro and hydroxyl groups in position 1 and 2, which lessens intermolecular interactions.

II - *o*-Nitrophenol has the lower melting point due to the asymmetry of the ring which makes this conformer less stable.

III - *p*-Nitrophenol has the higher melting point because it has more intermolecular hydrogen bond interactions.

IV - *p*-Nitrophenol has the higher melting point due to a large ring stability caused by the ring symmetry.

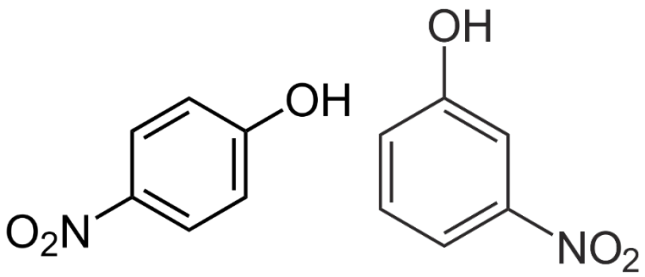
Choose only the correct affirmatives

a) I
b) II
c) I e III
d) II e IV
e) III

B) *o*-Nitrotoluene (M = 137,138 g mol^{-1}) has a very similar molar mass value compared to *o*-nitrophenol (M = 139,110 g mol^{-1}), but a lower melting point (F.P. = -10.4 °C). Describe the interactions that should be broken during the melting process for these compounds and point out the difference for the melting point values.

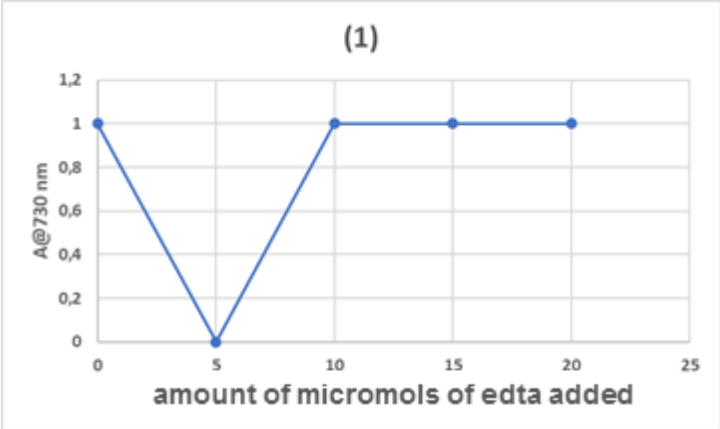
QUESTION 4

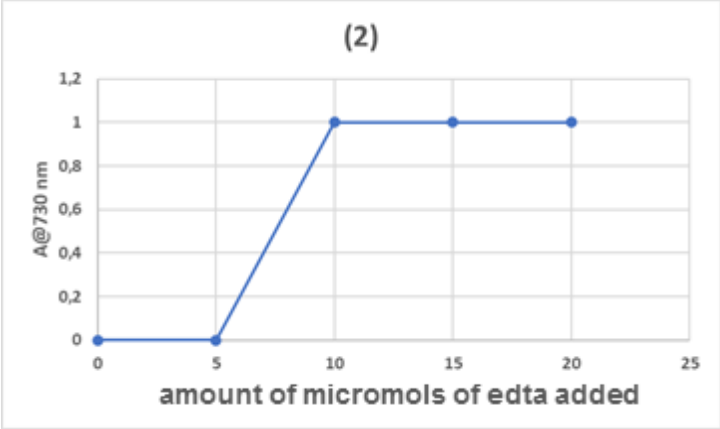
A) Still on nitrophenols, the *p*-nitrophenol and *m*-nitrophenol isomers (represented below) do not show significant absorption at 545 nm, but their respective conjugate bases do. Explain why.

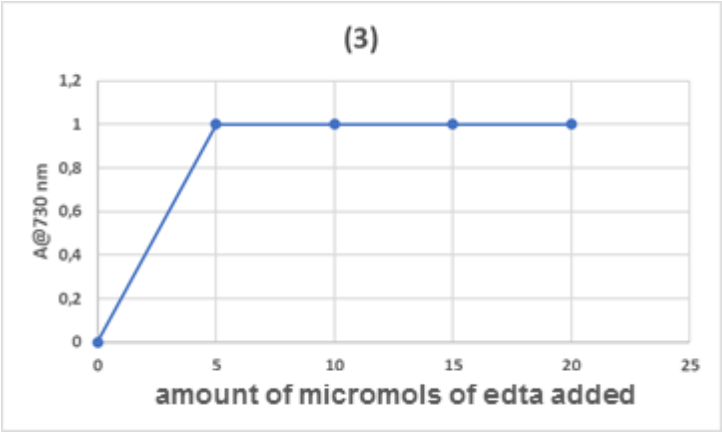


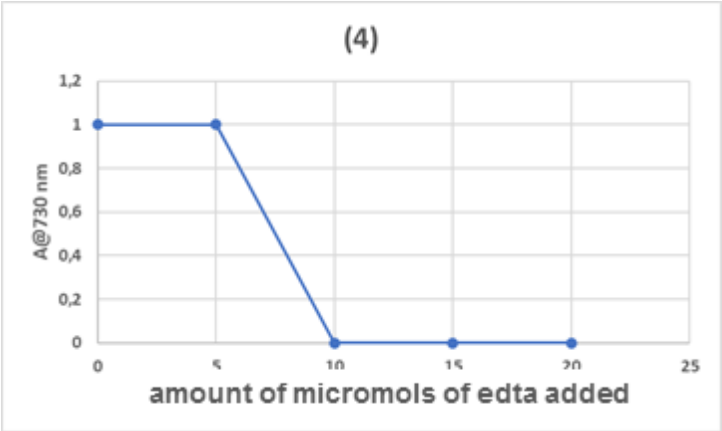
B) A 10.0 mL aliquot of a mixture of Bi^{3+} and Cu^{2+} ions (each at 0.5 millimolar) was titrated with edta from a concentrated solution that did not significantly change the volume of the final solution. Assuming that only the Cu(edta) complex exhibits absorbance at 730 nm, which scheme below best represents this titration curve?

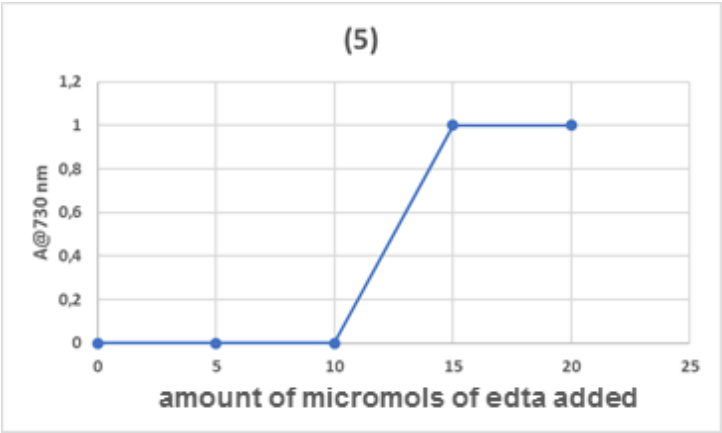
Data: M + edta ⇌ [M(edta)] log K = 19 (for M = Cu) or 28 (for M = Bi).






(3)
A@730 nm
1,2
1
0,8
0,6
0,4
0,2
0
0
5
10
15
20
25
amount of micromols of edta added


(4)
A@730 nm
1,2
1
0,8
0,6
0,4
0,2
0
0
10
25
amount of micromols of edta added


(5)
A@730 nm
1,2
1
0,8
0,6
0,4
0,2
0
0
5
10
15
20
25
amount of micromols of edta added

a) 1
b) 2
c) 3
d) 4
e) 5

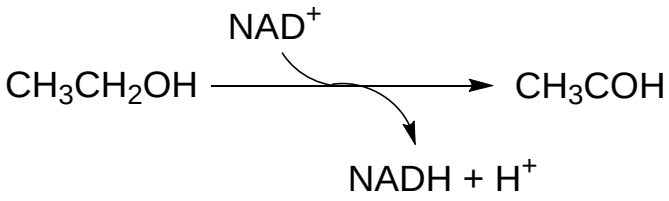
QUESTION 5

A) The formation of NOCL occurs in the presence of NO and of a large excess of Cl_2. This reaction follows a kinetics of second order. The reaction started from 300 Pa of NO and after 522 s the partial pressure of NOCl rose from 0 to 100 Pa. What is the rate constant for this reaction?

Choose the correct alternative:

a) $6{,}4 \times 10^{-6}$ Pa.s^{-1}
b) $1{,}7 \times 10^{-6}$ Pa.s^{-1}
c) $3{,}2 \times 10^{-6}$ Pa.s^{-1}
d) 4×10^{-5} Pa.s^{-1}
e) 2×10^{-4} Pa.s^{-1}

A) The alcohol dehydrogenase is one of the enzymes responsible for metabolization of ethanol to acetaldehyde in the presence of NAD^+. Calculate (in g.dm^{-3}min^{-1}) the conversion rate of ethanol to acetaldehyde when the ethanol concentration drops from 1.5 g.dm^{-3} to half in 49 minutes of reaction. Consider that the reaction kinetics is first order and that the concentration of NAD+ remains practically constant throughout the reaction:



QUESTION 6

A) The dissociation constant of NH_4OH is 1.75×10^{-5} and the ionization constant of water is 1.0×10^{-14}. Based on this information, which of the indicators below minimizes the end-point titration error of a titration of 25.00 mL of 0.10 mol L^{-1} NH_4OH with 0.10 mol L^{-1}HCl; Explain your choice.

- Bromothymol blue; transition range: 6.6 (yellow) to 7.6 (blue)
- Phenolphthalein; transition range: 8 (colorless) to 10 (pink)
- Methyl red; transition range: 4.4 (red) to 6.2 (yellow)

B) The solution obtained by dissolving 0.010 mol of NH_4Cl and 0.010 mol of NH_4OH in 1.0 L of water has a pH of 9.24.

I. Addition of 0.010 mol of NaOH to this solution causes a pH variation of +1.5 pH units (consider no volume changes).
II. Addition of 0.0010 mol of HCl to this solution causes a variation of –0.08 to -0.09 pH units (consider no volume changes).
III. Addition of 0.0010 mol of NaOH to this solution changes its pH to 9.50 (consider no volume changes).
IV. This is a buffer solution; therefore, its pH does not change by adding strong acids or bases.

Choose the correct alternative:

a) Statements I and IV are correct
b) Statements I, II, and IV are correct
c) Only statement IV is correct
d) Statements I and II are correct
e) Statements II and III are correct

QUESTION 7

U^{4+} ions can be quantified, in an acidic medium, using potentiometric titration with a standard solution of Ce^{4+} ions. The concentration of H^{+} in the medium remains at 1.0 $molL^{-1}$ throughout the experiment.

A) The reaction between these species gives rise to an electrochemical cell. When the titration reaches the stoichiometric point, we can say that:

a) The system behaves like a galvanic cell and the equilibrium potential when the stoichiometric point is reached is +1.07V
b) The system behaves like an electrolytic cell and the equilibrium potential when the stoichiometric point is reached is +1.10V
c) The system behaves like a galvanic cell and the equilibrium potential when the stoichiometric point is reached is +0.703V
d) The system behaves like a galvanic cell and the equilibrium potential when the stoichiometric point is reached is +1.05V

B) 2. Describe down the complete reaction properly balanced and indicate which electrodes and equipment you would use to perform this titration.

Data: $E°= (UO_2^{2+}/U^{4+}) = +0.334V$ and $E°(Ce^{4+}/Ce^{3+}) = +1.44V$
Nernst equation: $E = E° + RT/nF \ln[ox]/[Red]$

QUESTION 8

A) Consider the following affirmatives:

I. The entropy changing of the system (ΔS_{system}) in a reversible process is equal to the change in an irreversible process.

II. The entropy ($S = k_B \ln W$, where k_B is the Boltzmann constant and W is the number of microstates) of any substance at 0 K is zero.

III. The 1st Law of Thermodynamics says that $\Delta E_{universe} = 0$, while the 2nd Law says that $\Delta S_{universe} > 0$.

IV. A spontaneous process is always irreversible.

Among the following alternatives, choose the one that has only correct affirmatives:

a) I, III
b) II, III e IV
c) II e III
d) I, III e IV
e) I, II e III

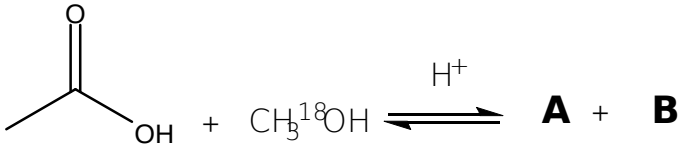
B) Some introductory textbooks of thermodynamics use the erroneous idea of "increasing of disorder" to explain the increasing of entropy in a spontaneous process. It is well known that is perfectly possible, in certain conditions, to obtain super cooled water, i.e. water in liquid state even in negative temperatures (-20ºC, for example). When there is a perturbation of the water in these conditions (e.g. mechanical shock), the spontaneous crystallization takes place forming ice, i.e. a more ordered arrangement of the water molecules. Based on the 2nd Law of thermodynamics explain in details why such crystallization is spontaneous and state if ΔG, ΔH e ΔS are <, = or > than zero in this process.

Data: $\Delta G = \Delta H - T\Delta S$

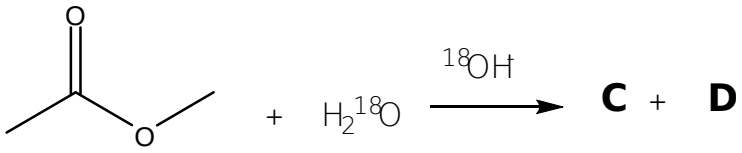
QUESTION 9

The reactions (i) and (ii), represented bellow, involve compounds labelled with ^{18}O.

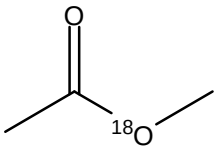
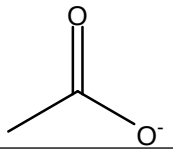
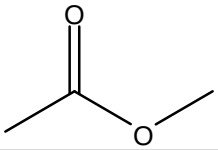
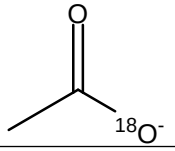
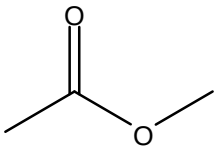
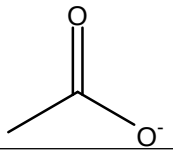
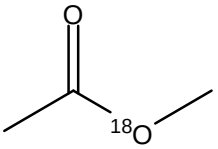
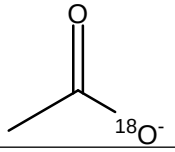
(i)



(ii)



A) Which of the alternatives bellow show the products A and B, for reaction (i), and C and D, for reaction (ii), respectively?

	Compound A	Compound B	Compound C	Compound D
a)		H_2O		$CH_3{}^{18}OH$
b)		$H_2{}^{18}O$		CH_3OH
c)		$H_2{}^{18}O$		$CH_3{}^{18}OH$
d)		H_2O		CH_3OH
e)	None of the above alternatives is correct			

B) Explain your answer for item A, based on the mechanisms of reactions (i) and (ii).