

Name:

Code:

3rd Nordic Chemistry Olympiad

Theoretical Problems

18th July 2018
Oslo, Norway

Instructions

- Write your name and country code on all pages.
- The test booklet consists of 6 tasks and 29 pages.
- You have 5 hours for the examination. Do not start until the "START" signal is given.
- Use only the ballpoint pen and the calculator that have been handed out.
- Read the entire task before you begin to solve it, as there may be important information at the end of the text that you need to use to solve the task.
- All results must be written within the boxes. Answers written outside the boxes will not be reviewed and corrected. If you need paper, use the back of the paper sheets.
- Show your calculations in the boxes. You will only get max points if you show your calculations.
- When you have finished the exam, you must pass the test booklet to the person in charge.
- You must stop writing when the "STOP" signal is given.
- Stay in your place until you are allowed to leave the room.

Constants and Formulae

Avogadro's constant, $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant, $k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1}$

Universal gas constant, $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08205 \text{ atm L K}^{-1} \text{ mol}^{-1}$

Speed of light, $c = 2.9979 \times 10^8 \text{ m s}^{-1}$

Planck's constant, $h = 6.6261 \times 10^{-34} \text{ J s}$

Faraday constant, $F = 9.64853399 \times 10^4 \text{ C}$

Mass of electron, $m_e = 9.10938215 \times 10^{-31} \text{ kg}$

Standard pressure, $P = 1 \text{ bar} = 10^5 \text{ Pa}$

Atmospheric pressure, $P_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr}$

Zero of the Celsius scale, 273.15 K

1 picometer (pm) = 10^{-12} m ; 1 Å = 10^{-10} m ; nanometer (nm) = 10^{-9} m

1 eV = $1.6 \times 10^{-19} \text{ J}$

1 amu = $1.66053904 \times 10^{-27} \text{ kg}$

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U - PV$

Gibbs free energy: $G = H - TS$ $\Delta G = \Delta G^\circ + RT \ln Q$

$$\Delta G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$$

Entropy change: $\Delta S = \frac{q_{\text{rev}}}{T}$, where q_{rev} is heat for the reversible process

$$\Delta S = nR \ln \frac{V_2}{V_1} \text{ (for isothermal expansion of an ideal gas)}$$

Nernst equation: $E = E^\circ + \frac{RT}{nF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$

Energy of a photon: $E = \frac{hc}{\lambda}$

Lambert-Beer law: $A = \log \frac{I_0}{I} = \epsilon b C$

Integrated rate law

Zero order $[A] = [A]_0 - kt$ First order $\ln [A] = \ln [A]_0 - kt$

Second order $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Arrhenius equation

$$k = Ae^{-E_a/RT}$$

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Periodic table of the elements with relative atomic masses and electronegativities

1	1,00794																	2	4,0026																																
H																		He																																	
2,1																																																			
3	6,941	4	9,0121																	5	10,811	6	12,011	7	14,007	8	15,999	9	18,998	10	20,180																				
Li		Be																		B		C		N		O		F		Ne																					
1,0		1,5																		2,0		2,5		3,0		3,5		4,0																							
11	22,990	12	24,305																	13	26,982	14	28,086	15	30,974	16	32,066	17	35,453	18	39,948																				
Na		Mg																		Al		Si		P		S		Cl		Ar																					
0,9		1,2																		1,5		1,8		2,1		2,5		3,0																							
19	39,098	20	40,078	21	44,956	22	47,87	23	50,942	24	51,996	25	54,938	26	55,845	27	58,933	28	58,693	29	63,546	30	65,39	31	69,723	32	72,61	33	74,922	34	78,96	35	79,904	36	83,80																
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr																	
0,8		1,0		1,3		1,5		1,6		1,6		1,5		1,8		1,9		1,9		1,9		1,6		1,6		1,8		2,0		2,4		2,8																			
37	85,468	38	87,62	39	88,906	40	91,224	41	92,906	42	95,94	43	(97,907)	44	101,07	45	102,91	46	106,42	47	107,87	48	112,41	49	114,82	50	118,71	51	121,76	52	127,60	53	126,90	54	131,29																
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe																	
0,8		1,0		1,2		1,4		1,6		1,8		1,9		2,2		2,2		2,2		1,9		1,7		1,7		1,8		1,9		2,1		2,5																			
55	132,91	56	137,33	57	138,91	72	178,49	73	180,95	74	183,84	75	186,21	76	190,23	77	192,22	78	195,08	79	196,97	80	200,59	81	204,38	82	207,20	83	208,98	84	(209)	85	(210)	86	(222)																
Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn																	
0,7		0,9		1,0		1,3		1,5		1,7		1,9		2,2		2,2		2,2		2,4		1,9		1,8		1,9		1,9		2,0		2,2																			
87	(223)	88	(226)	89	(227)	104	(261)	105	(262)	106	(263)	107	(262)	108	(265)	109	(266)																																		
Fr		Ra		Ac		Rf		Db		Sg		Bh		Hs		Mt																																			
0,7		0,7																																																	
																						58	140,12	59	140,91	60	144,24	61	(144,91)	62	150,36	63	151,96	64	157,25	65	158,93	66	162,50	67	164,93	68	167,26	69	168,93	70	173,04	71	174,97		
																						Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu			
																						90	232,04	91	231,04	92	238,03	93	(237,05)	94	(244,06)	95	(243,06)	96	(247)	97	(247,07)	98	(251,08)	99	(252,08)	100	(257,1)	101	(258,1)	102	(259,1)	103	(262,1)		
																						Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr			

Problem 1

10 % of total

a	b	c	d	e	f	g	h	Problem 1	%
10	10	10	10	10	10	10	10	80	10

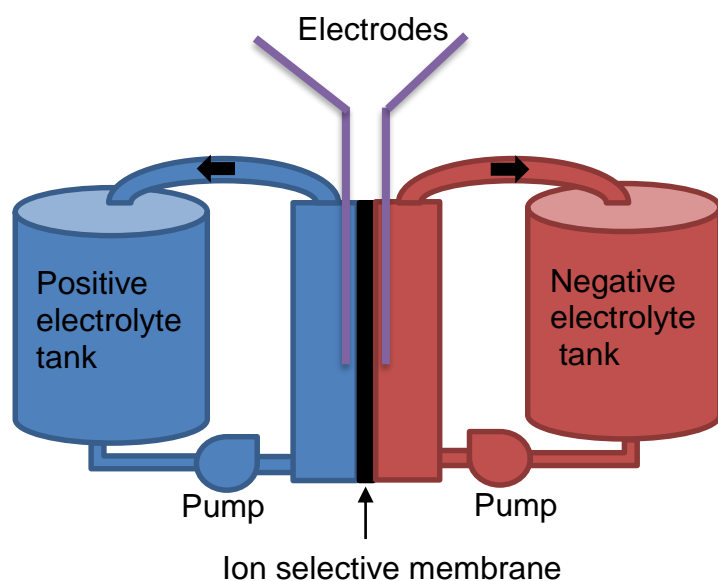
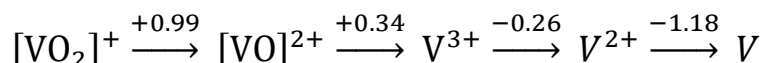


Figure 1, left: Schematic of redox flow battery. Right: 4 MWh containerized vanadium flow battery.

In the hunt for better solutions for energy storage, the redox flow batteries have recently had a resurgence in interest. The battery is comprised of two reaction chambers separated by a membrane with each chamber connected to an electrode and to a tank for storage of electrolyte. The most common of these is the vanadium redox battery.

During discharge the vanadium goes from V(V) to V(IV) in the positive electrolyte tank and from V(II) to V(III) in the negative electrolyte tank. The potential diagram for vanadium at pH = 0 is given below.



- a) Write the balanced equations for the anode and cathode reactions during discharge

Anode:

Cathode:

- b) What will the standard electrode potential of the cell be?

$E^0 =$

- c) Assume that the cathode half cell of the vanadium redox battery is connected to a standard hydrogen half cell ($E^0 = 0$). At what pH will the cathode reaction stop being spontaneous? Assume standard pressure and 25 °C and 1.0 mol/L for all vanadium species.

pH =

A new vanadium redox battery is being built in China (scheduled completion 2019) that can deliver 200 MW for 4 hours.

- d) Assume that the voltage stays at E^0 and the battery is 90% discharged at the end. How many liters of 1.0 mol/L battery solution is needed for the cathode?

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Liters of solution:

- e) What will the actual potential of the battery at 90 % discharge (assume 1.0 mol/l of all constituents at starting point and constant pH = 0). Assume 25 °C.

- f) The electrolyte containing V(V) is made by dissolving V_2O_5 in sulphuric acid. Write the balanced equation for the solvation.

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- g) There is a leak! Suggest a balanced reaction for what happens when the two electrolytes meet. Assume equal molar amounts of each electrolyte.

- h) What happens if a leak in a fully discharged battery mixes the two electrolytes?

Problem 2

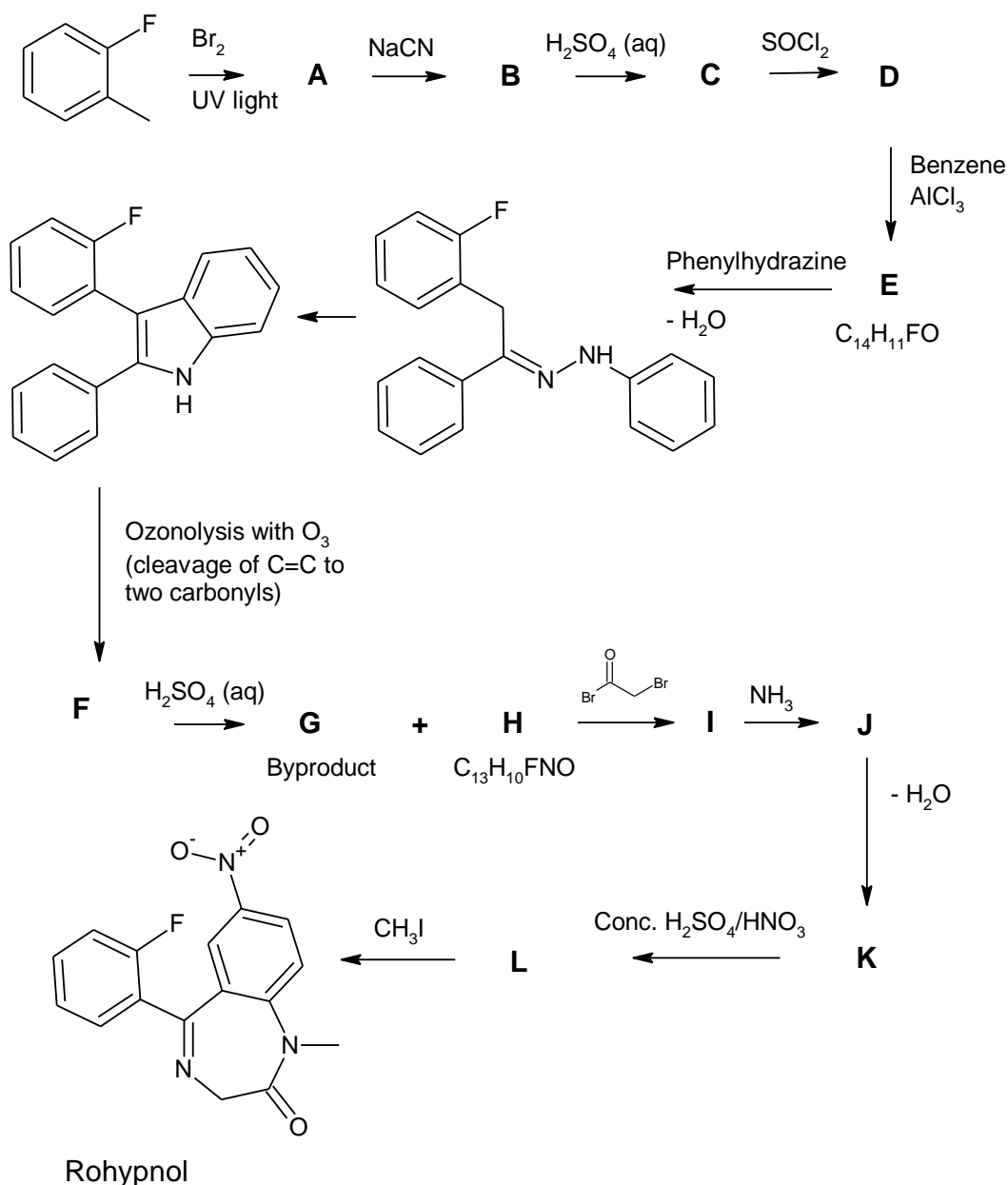
10 % of total

a	b	c	d	e	f	g	h	i	j	k	Problem 2	x %
10	10	10	10	10	10	10	10	10	10	10	110	10

Rohypnol is a benzodiazepine used in some countries to treat severe insomnia as well as being used in anesthesia.

As for other hypnotic drugs the use of Rohypnol should be limited to short-term use or on an occasional basis by those with chronic insomnia.

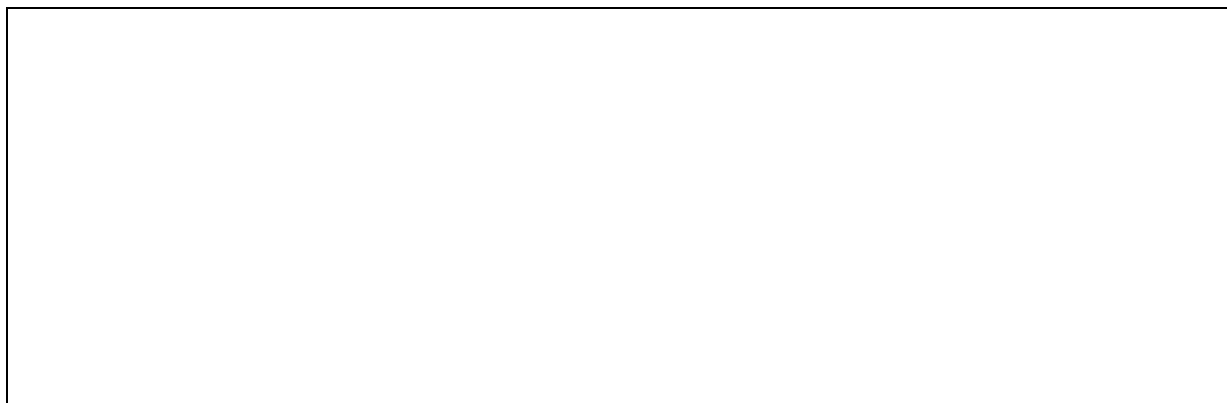
One way to make Rohypnol is illustrated in the scheme below:



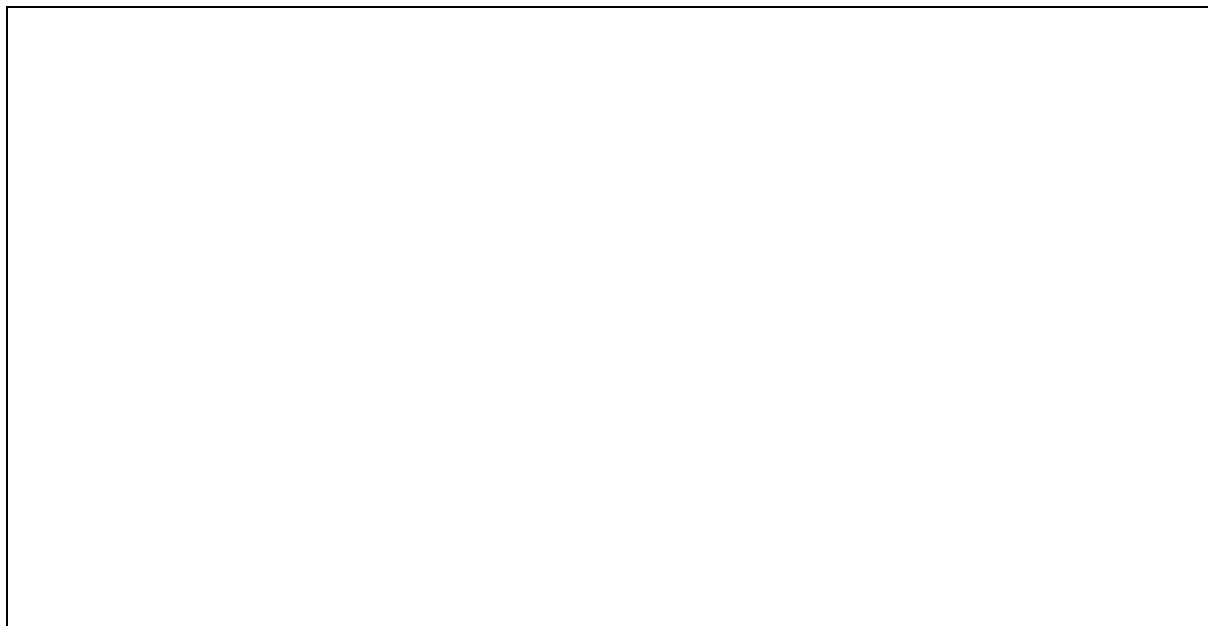
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a) The first step is to make **A**. It is done by a substitution on the aliphatic carbon. Draw the structure of **A**.



b) Draw the structure of **B** and draw a suggestion for the mechanism



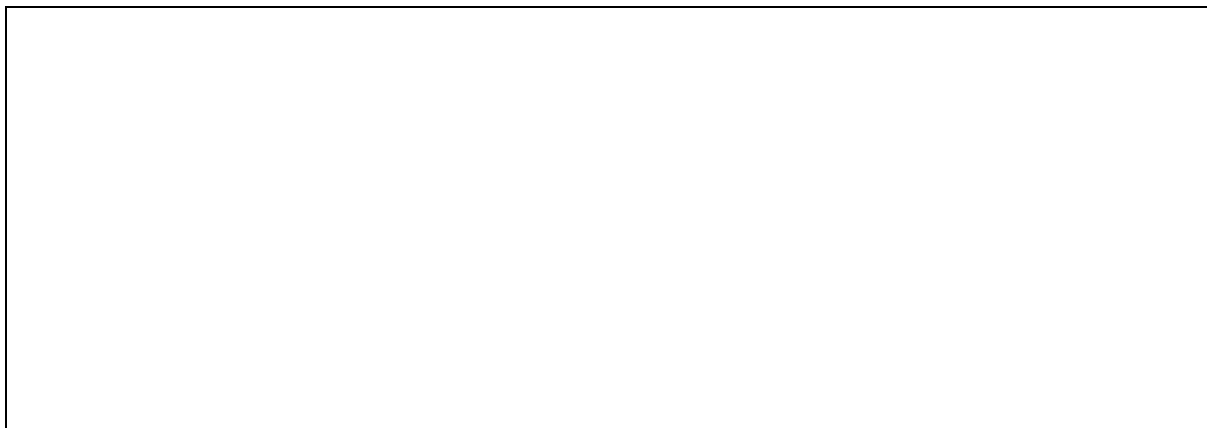
c) Draw the structure of **C**.



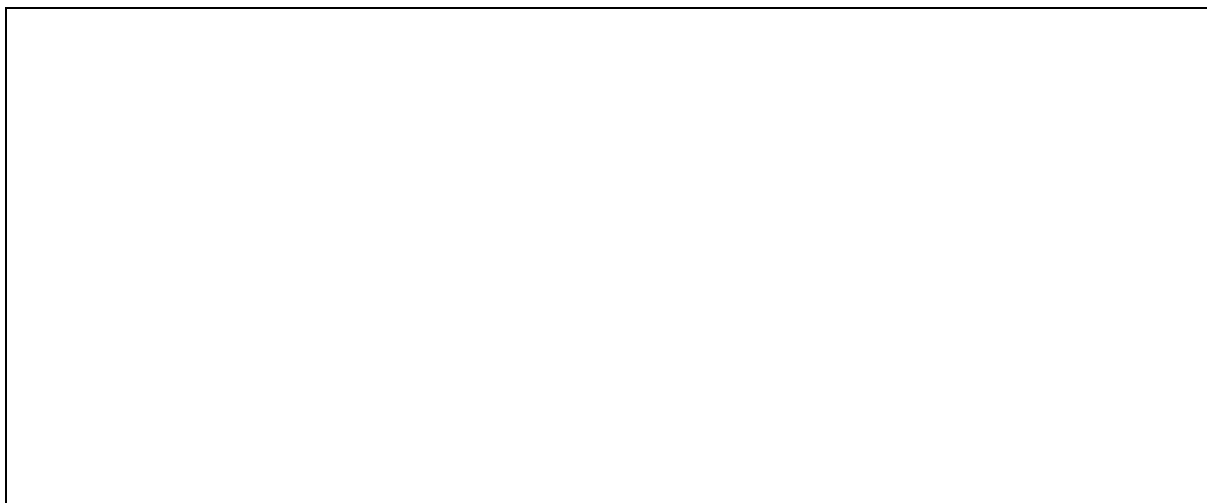
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d) Draw the structure of **D**.



e) Draw the structure of **E**.



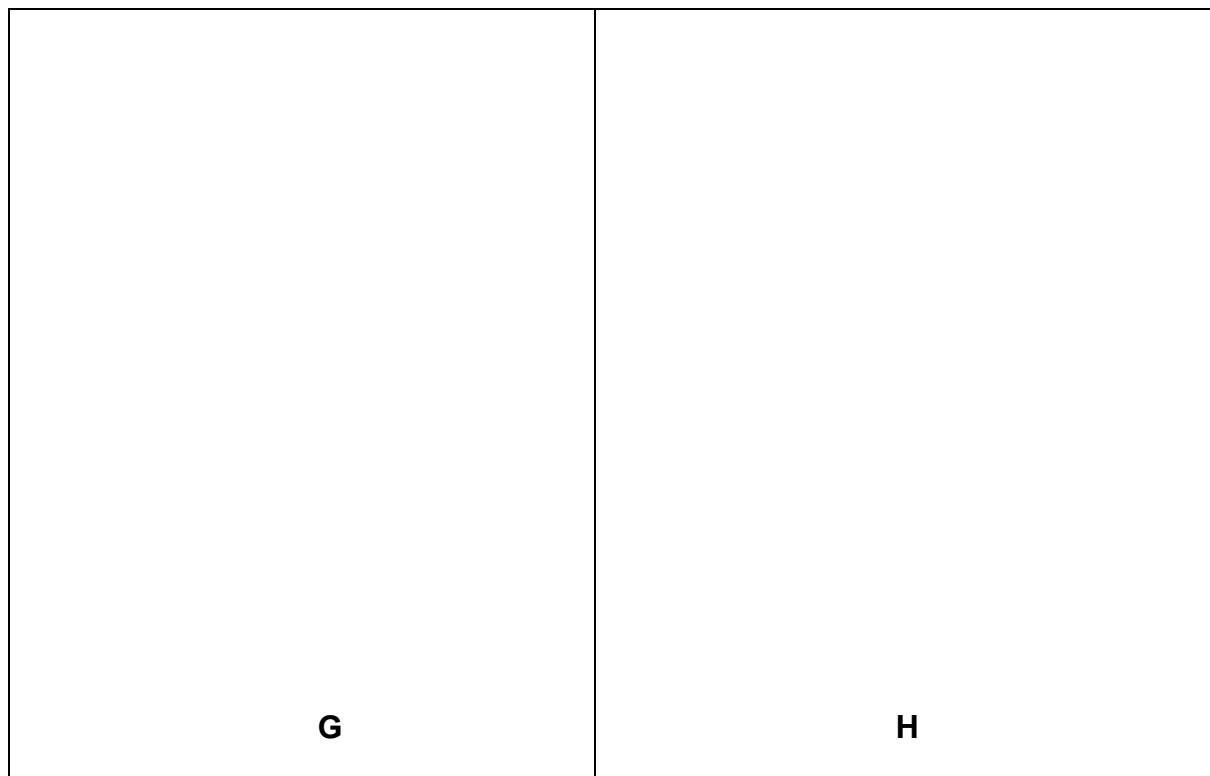
f) After ozonolysis, **F** containing three benzene rings was obtained. Draw the structure of **F**.



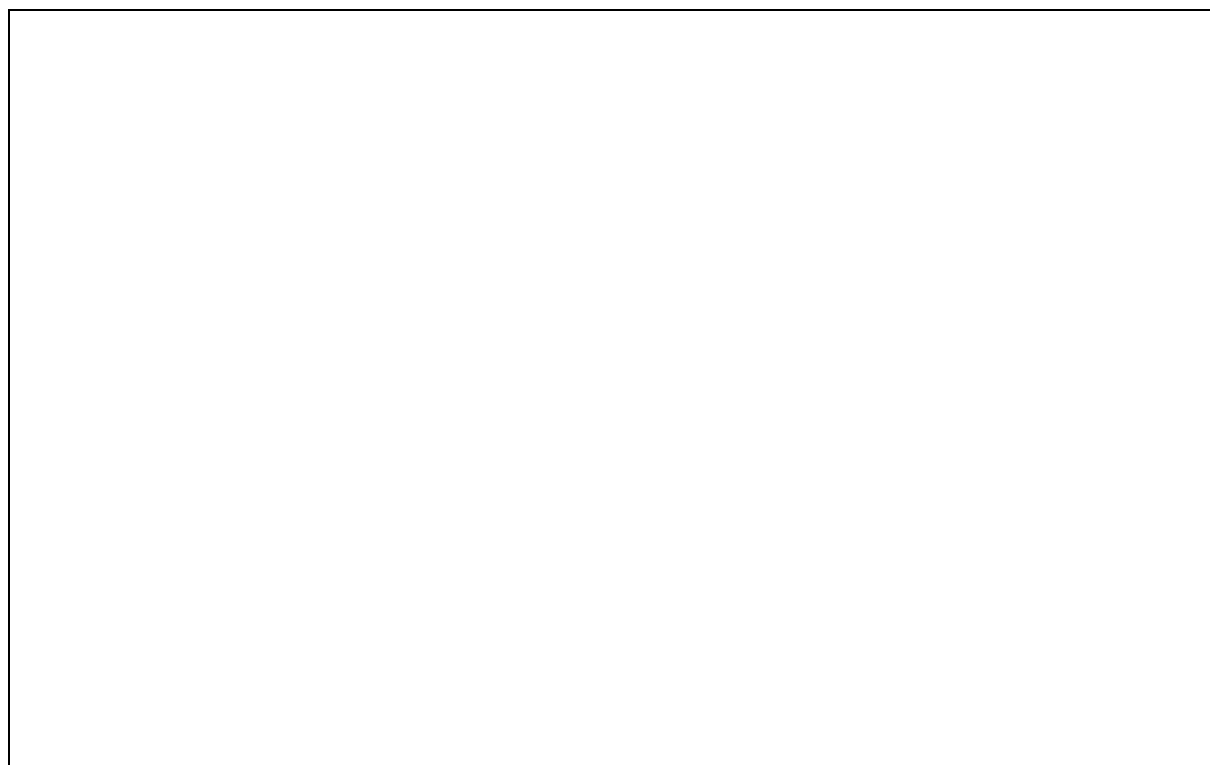
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g) **F** can be cleaved by hydrolysis with diluted H_2SO_4 . Draw the structures of **G** and **H**.



h) Draw the structure of **I**.



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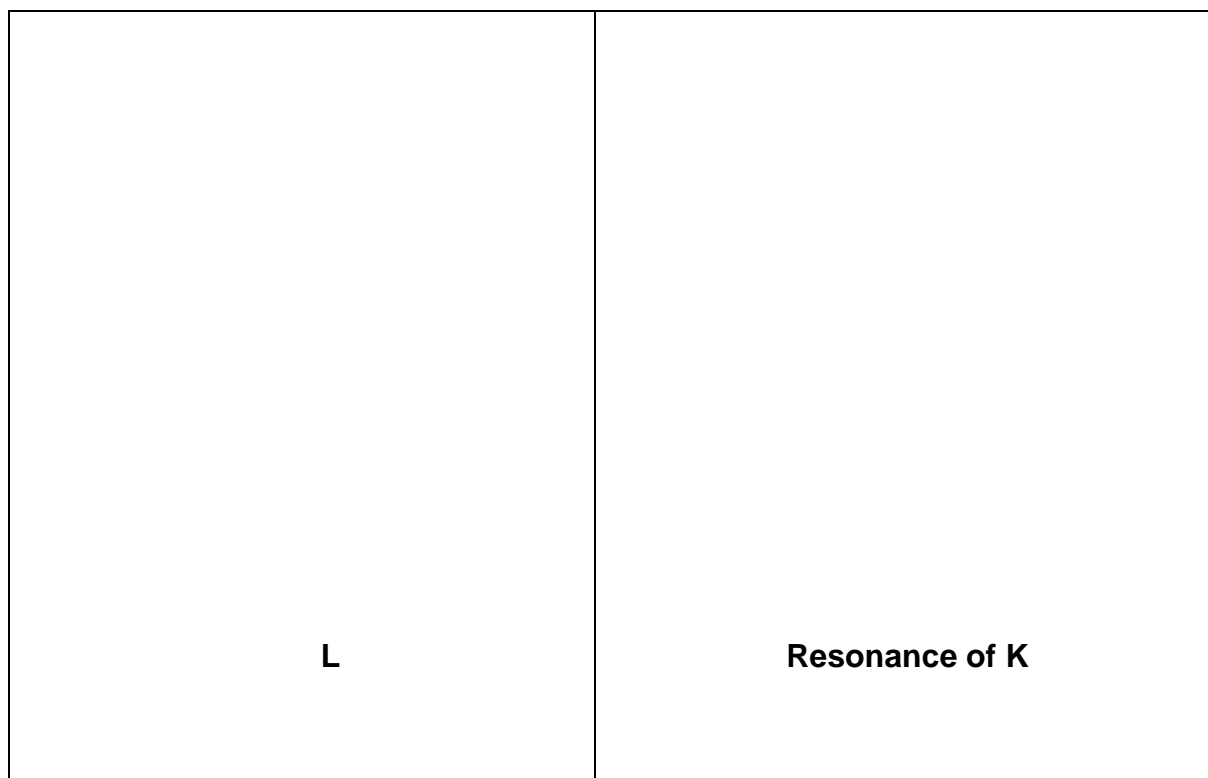
i) Draw the structure of **J**.



j) Draw the structure of **K**.



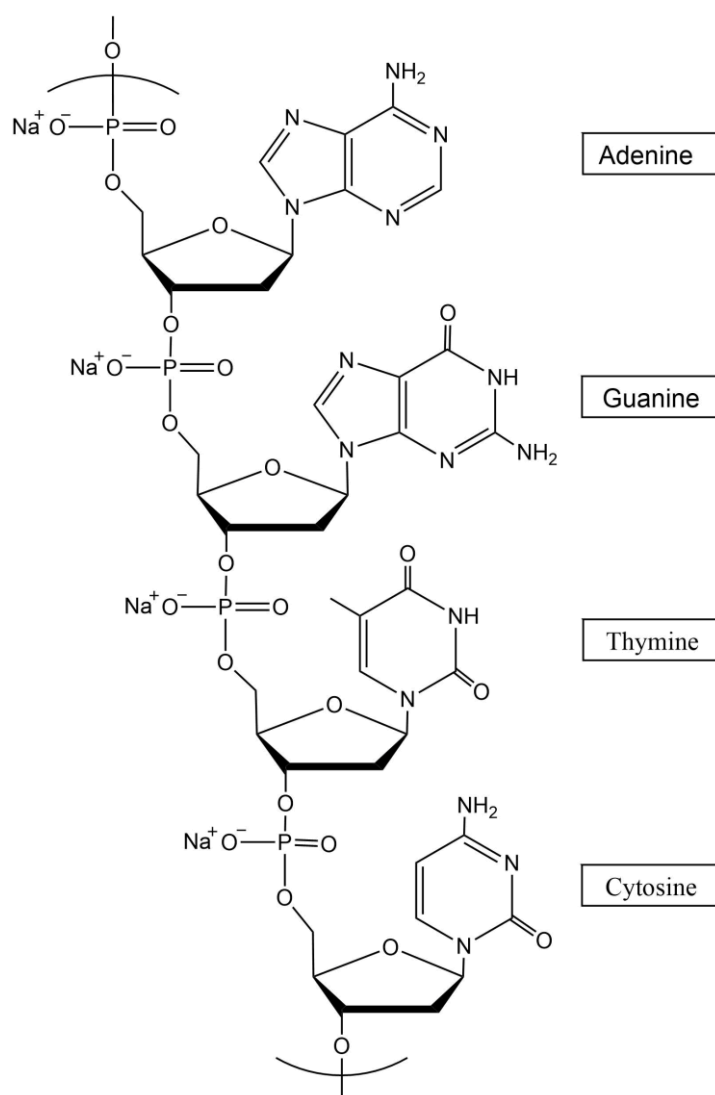
k) Draw the structure of **L**, and draw a resonance structure of **K** that can explain the obtained product.



Problem 3**10 % of total**

a	b	c	d	e	f	g	Problem 3	%
10	10	10	10	10	10	10	70	10

A DNA (2'-deoxyribonucleic acid) strand is an unbranched polymer of repeating nucleotides. Each nucleotide consists of a heterocyclic, nitrogen-containing base, a five-carbon sugar (ribose) and a phosphate group. The DNA segment shown is (5')AGTC(3') and has a formula mass of 1323,72 g/mol.



a) Assuming that equimolar amounts of the four bases are present in DNA, write the number of H-atoms per P-atoms. Calculate (to 3 significant figures) the theoretical mass percentage of H expected upon elemental analysis of DNA.

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Mass % H:

The most common hydrogen-bonding patterns are those defined by James D. Watson and Francis Crick in 1953, in which A bonds specifically to T, and G bonds to C. This means that the complementary DNA segment to the segment shown in the picture is (5')GACT(3')

b) One strand of a double-helical DNA has the sequence (5')GCGCAATATTTC(3'). Write the base sequence of the complementary strand.

c) Draw the structural formula of the two standard DNA base pairs and indicate the hydrogen bonds. The sugar-phosphate backbone can be abbreviated as (-R).

d) The base composition of DNA generally varies from one species to another. In samples of DNA isolated from two unidentified species of bacteria, X and Y, adenine makes up 32 % and 17 % respectively, of the total bases.

- I. What relative proportions of adenine, guanine, thymine and cytosine would you expect to find in the two DNA samples?
- II. One of these species was isolated from a hot spring (64 °C). Which species (X or Y) is most likely the thermophilic bacterium and why?

I.	II.
----	-----

e) The DNA double helix in the human body has a mass of about 10^{-18} g per 1000 nucleotide pairs; each base pair extends 3.4 Å.

- I. Calculate the mass in grams of a double helical DNA molecule stretching from the Earth to the Moon (320000 km).
- II. Your body contains about 45 gram of DNA. How many times could you stretch your DNA from the Earth to the Moon and back (640000 km)?

Name:

Code:

I.	II.
----	-----

- f) The DNA is constantly threatened by internal and external sources that can damage the molecule, including reactive oxygen species, other reactive radicals, as well as various types of ionizing radiation such as UV-radiation. All bases are affected and for adenine, the exocyclic amine group is vulnerable to oxidation. The amine is converted into a ketone. The base that is formed by this oxidation of adenine is called *inosine*. Draw the structure of the base part of *inosine* (you can skip drawing the sugar-phosphate backbone, just indicate the link/position with an R-group)

--

g) *Inosine* has different base-pairing properties than adenine, and prefer to base-pair with other bases than the thymine that was originally pairing with the adenine.

- I. How many of the hydrogen bonds between A and T in the original base pair are disrupted if adenine is oxidized to *inosine*?
- II. Which of the three remaining bases (A, C or G) do you think form the most stable base pair with *inosine*? Draw the base pair showing the hydrogen bonding pattern.

I.	II.
----	-----

Problem 4**10 % of total**

a	b	c	d	e	f	g	Problem 4	x %
10	10	10	10	10	10	10	70	10

Elemental zinc is a common reductant and chlorine-water a common oxidant in qualitative inorganic analysis. In this task the reaction that occurs when elemental zinc is put into chlorine-water is considered from the thermodynamic point of view. Furthermore, the manufacture and stability of chlorine-water is considered.

The standard reduction potentials are as follows (25.00 °C):



The standard third-law entropies are as follows (25.00 °C):



The standard state of gases is 1 bar = 100 000 Pa partial pressure.

Let us first consider the reaction of elemental zinc with chlorine-water:



a) Calculate the standard reaction Gibbs's energy $\Delta_r G^{\circ}$ for the reaction at 25.00 °C.

$\Delta_r G^{\circ} =$

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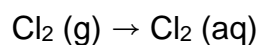
b) Calculate the standard reaction enthalpy $\Delta_r H^\circ$ for the reaction at 25.00 °C

$\Delta_r H^\circ =$

c) Calculate the standard cell voltage E° for the reaction at 75.00 °C. You may assume that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ do not depend on temperature.

$E^\circ =$

Let us then consider the dissolution of chlorine into water:



d) Calculate the equilibrium constant k_H for the reaction, i.e. the Henry's law constant for chlorine, at 25.00 °C.

 $K_H =$

e) Calculate the concentration of chlorine in water at equilibrium when a mixture of 0.200 mol chlorine gas and 1.00 L water is sealed into a 2.00 L flask at 25 °C. If you did not find a value for k_H in d), you can use $k_H = 0.214$.

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$[\text{Cl}_2] =$

Finally, let us consider how the concentration of the chlorine-water decreases when the above flask is opened, i.e. how the chlorine-water becomes flat. We consider the effect of opening the flask to be such that all chlorine gas is removed but no chlorine from the solution is neither removed nor entered into the gas phase. No water is removed from the flask, and the temperature remains constant. After resealing the flask a new equilibrium is established, i.e. chlorine is entered from the solution into the gas phase.

f) Calculate the concentration of chlorine in water after the flask has been opened once.

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g) How many times of opening the flask causes the concentration of chlorine in water to become less than 10 % of the original?

Problem 5**10 % of total**

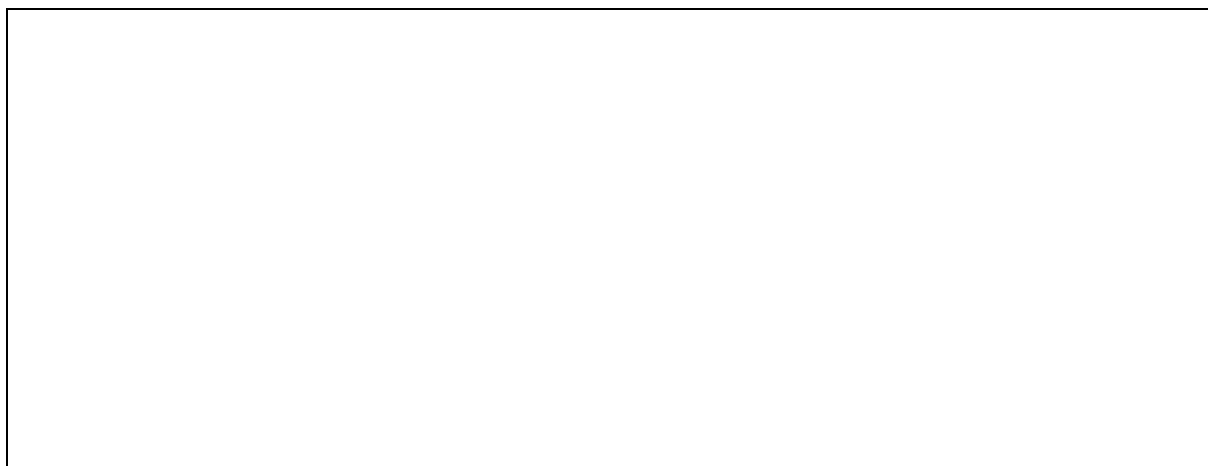
a	b	c	d	e	f	g	h	Problem 5	%
10	10	10	10	10	10	10	10	80	10

Carbonic acid, H_2CO_3 is an elusive species, for long not thought to exist in pure state. Although the pure state is now known to exist under special circumstances, we normally have to consider a range of species including CO_2 (aq), CO_2 (g), HCO_3^- , CO_3^{2-} , H_2O , H^+ and OH^- when discussing the chemistry of carbonic acid.

a) Draw the Lewis structure for H_2CO_3 , indicating all valence electrons for all atoms.



b) Theoretically adding carbonic acid to water will create an equilibrium between H_2CO_3 , CO_2 and H_2O . Write a balanced equation for the equilibrium between these three species.



The ratio between dissolved carbonic acid and dissolved carbon dioxide in water is given by the hydration equilibrium constant, $K_H = [\text{H}_2\text{CO}_3]/[\text{CO}_2]$ is $1.7 \cdot 10^{-3}$ in pure water.

c) What species is the dominating carbon species only considering the simple equilibrium from task b)?

The simple equilibrium above does not tell the full story. Carbonic acid is a diprotic acid, with the following dissociation constants:

$$K_{a1} = 2.5 \cdot 10^{-4}$$

$$K_{a2} = 4.69 \cdot 10^{-11}$$

As $K_{a1} \gg K_{a2}$, it is clear that CO_3^{2-} can be disregarded for all practical purposes.

d) Disregarding formation of CO_2 , what is the pH of a 0.1 mol/L solution of H_2CO_3 ?

pH =

Finally, the concentration of dissolved CO_2 is highly dependent on the partial pressure of CO_2 on the surface of the solution, given by Henry's constant as:

$$k_H = \frac{p_{\text{CO}_2}}{[\text{CO}_2]} = 29.76 \text{ atm}/(\text{mol/L})$$

e) With a typical p_{CO_2} of $4 \cdot 10^{-4}$ atm at the surface of the earth, what will be the typical concentration of dissolved CO_2 in a glass of pure water?

[CO₂] =

With all these expressions at hand, for K_{a1} , K_H , k_H , in addition to charge neutrality:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

and the self-ionization of water:

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

we can paint the full picture of carbonic acid in water.

f) Show that the composition of the solution is fully determined by p_{CO_2} by finding an expression for $[\text{H}^+]$ that has p_{CO_2} as the only variable. You may disregard CO_3^{2-} completely by saying that $[\text{CO}_3^{2-}] = 0$.

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[H⁺]=

g) If you leave a glass of pure water on the bench and let it reach equilibrium for the CO₂ (g), CO₂ (aq) and H₂CO₃ (aq) system. What will the pH be? If you did not find an expression for [H⁺] in task f), use $[H^+] = \left(\frac{K_H K_A}{k_h} p_{CO_2} \right)^{1/2}$.

pH =

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In a bottle of fizzy drinks, the CO_2 pressure over the liquid is typically 2.5 atm.

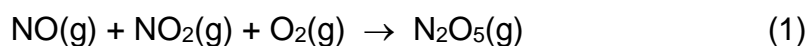
h) What is the dominant carbon species in such a drink?

Problem 6

10 % of total

a	b	c	d	e	Problem 4	%
10	10	10	10	10	50	10

Dinitrogen pentoxide, N_2O_5 , is a reactive molecule used as a nitrant in organic chemistry. When NO reacts with NO_2 and O_2 , N_2O_5 is formed according to reaction (1).



The following measurement data was obtained in an experimental series.

$[\text{NO}]_{\text{initial}}$ (mol/dm^3)	$[\text{NO}_2]_{\text{initial}}$ (mol/dm^3)	$[\text{O}_2]_{\text{initial}}$ (mol/dm^3)	Initial rate ($\text{mol}/(\text{dm}^3 \cdot \text{s})$)
0.20	0.30	0.20	$1.26 \cdot 10^{-1}$
0.10	0.10	0.20	$2.10 \cdot 10^{-2}$
0.10	0.10	0.10	$2.10 \cdot 10^{-2}$
0.20	0.10	0.10	$4.20 \cdot 10^{-2}$

a) Determine the reaction orders for NO, NO_2 and O_2 .

T

Reaction orders: NO:..... NO_2 :..... O_2 :...**0**.....

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b) Calculate the rate constant. Also give the unit of the rate constant.

Answer:

unit.....

The N_2O_5 molecule decomposes in the gas phase according to the net reaction (2)



The temperature dependence of the decomposition was studied and the following measurement data was obtained:

T (K)	k (s^{-1})
338	$4.9 \cdot 10^{-3}$
318	$5.0 \cdot 10^{-4}$
298	$3.5 \cdot 10^{-5}$

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c) Determine the mean activation energy of the reaction. Give your answer in kJ/mol.

Answer: $E_a =$ kJ

d) Calculate the mean frequency of the reaction (pre-exponential factor).

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- e) What is the half-life of decomposition of N_2O_5 at 402 K? (If you weren't able to calculate E_a and A in c) and d), use the values $E_a = 115 \text{ kJ}$ and $A = 3.6 \cdot 10^{14}$. These are however not the correct values)

Answer: $t_{1/2} =$

The end of the problem set