ANWEISUNGEN

- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem.
- Write all necessary calculations legibly.
- Put your pages into the provided envelope at the end of the exam. Do not stick down the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when allowed to do so.
- Only answers written on the answer sheets can be considered.
- This test has 18 pages.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

Constants and formulae

Avogadro constant	$N_A = 6.022 \cdot 10^{23}\,\text{mol}^{-1}$	Ideal gas equation	$pV = nRT$
Gas constant	$R = 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$	Gibbs energy	$G = H - TS$
Faraday constant	$F = 96485\,\text{C mol}^{-1}$	$\Delta_r G^0 = -RT \cdot \ln(K) = -nFE^0_{\text{Zelle}}$	
Planck constant	$h = 6.626 \cdot 10^{-34}\,\text{J s}^{-1}$	Nernst equation	$E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln\left(\frac{c_{\text{ox}}}{c_{\text{red}}}\right)$
Speed of light	$c = 2.998 \cdot 10^8\,\text{m s}^{-1}$	Energy of a photon	$E = \frac{h \cdot c}{\lambda}$
Temperature	$0\,°\text{C} = 273.15\,\text{K}$	Lambert-Beer law	$A = \log\left(\frac{I_0}{I}\right) = \epsilon \cdot c \cdot L$

For the calculation of equilibrium constants all concentrations refer to the standard concentration $1\,\text{mol dm}^{-3} = 1\,\text{mol l}^{-1}$. If not stated otherwise in a task, consider all gases ideal throughout this test.

Periodic table with relative atomic masses

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc –	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57–71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po –	85 At –	86 Rn –
87 Fr –	88 Ra –	89–103	104 Rf –	105 Db –	106 Sg –	107 Bh –	108 Hs –	109 Mt –	110 Ds –	111 Rg –	112 Cn –						

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm –	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac –	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np –	94 Pu –	95 Am –	96 Cm –	97 Bk –	98 Cf –	99 Es –	100 Fm –	101 Md –	102 No –	103 Lr –

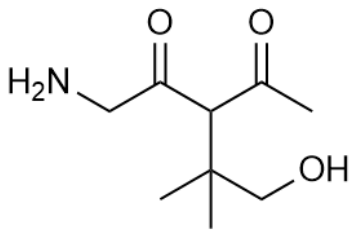
Problem 1 - Multiple choice **5 points**

Even if the question is put in the singular one or more answers may be correct.

a) Which of the following elements has the highest 1st ionization energy?
   - i) Li
   - ii) F
   - iii) N
   - iv) Ca
   - v) Cl

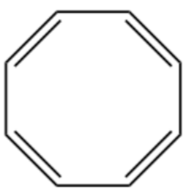
b) Which of the following elements has the smallest atom radius?
   - i) Br
   - ii) Be
   - iii) O
   - iv) C
   - v) Mg

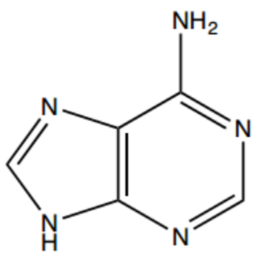
c) What is the IUPAC name of the molecule with the following structure?

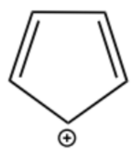


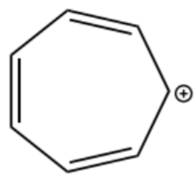
   - i) 1-Amino-3-(1-hydroxy-2-methylpropan-2-yl)-2,4-dipentone
   - ii) 3-(1-Hydroxy-2-methylpropyl)-1-aminopentane-2,4-dione
   - iii) 3-Acetyl-5-amino-1-hydroxy-2,2-dimethylpentane
   - iv) 3-(1-Hydroxy-2-methylpropan-2-yl)-1-aminopentane-2,4-dione
   - v) 1-Amino-3-(1-hydroxy-2-methylpropan-2-yl)pentane-2,4-dione

d) Which of the following are aromatic compounds?

i) 

ii) 

iii) 

iv) 

e) the water-gas shift reaction is a procedure used to reduce the amount of carbon monoxide in gases and to get hydrogen gas. The equilibrium is

$$CO + H_2O \rightleftharpoons CO_2 + H_2,\ \Delta_r H^0 = -41.2\,\mathrm{kJ\,mol^{-1}}$$

Which of the following statements are true?

i) With increasing temperature the equilibrium shifts to the reactants

ii) With increasing temperature the equilibrium shifts to the products

iii) With increasing pressure the equilibrium shifts to the reactants

iv) With increasing pressure the equilibrium stays the same

v) With increasing pressure the equilibrium shifts to the products

f) One can make the following statements about the change in entropy upon dissolution of a salt in water (process 1) and dissolution of a gas in water (process 2):

i) The entropy increases for 1 and 2

ii) The entropy decreases for 1 and 2

iii) The entropy increases for 1 and decreases for 2

iv) The entropy decreases for 1 and increases for 2

Problem 2 - Short questions 6.5 points

a) Aluminium sulfide can be obtained by a strongly exothermic reaction from aluminium and sulfur. What is the molecular formula of the compound?

b) Explain for the following mixtures of solvents which are well mixable and why?

i) Water - Heptane

ii) Heptane - Ethanol

iii) Acetone - Water

c) Consider the combustion of magnesium in oxygen:

$$2\ \mathrm{Mg} + \mathrm{O_2} \rightarrow 2\ \mathrm{MgO}$$

What quantity of oxygen gas is needed for 10 g of amgnesium?

d) Draw the three-dimensional molecular structure of SCl_2, $[IF_4]^+$ and Al_2Cl_6. Write down the oxidation state as well as the valency of the central atom.

e) Draw the constitutional formula of the following molecules:

i) (*E*)-4-Methylhex-2-ene

ii) Penta-1,4-dien-3-one

iii) 3-Methylenpenta-1,4-diene

iv) (*E*)-*N*-Ethyl-4,4-dimethylpent-2-enamide

Problem 3 - Acids and bases **7 points**

Calculate the pH values of the following aqueous solutions:

a) 1 mmol sodium hydroxide (NaOH) in 100 ml water.

b) 1 g pyridine (C_5H_5N, $pK_b = 8.7$) in 100 ml water.

c) 1 g iron(II)chlorid-tetrahydrate ($FeCl_2 \cdot 4\ H_2O$, $pK_a = 6.7$) in 100 ml water.

d) 1 g iron(III)chloride-hexahydrate ($FeCl_3 \cdot 6\ H_2O$, $pK_a = 2.2$) in 100 ml water.

e) State with a stoichiometric equation why a solution containing iron(III)chloride is acidic.

Problem 4 - Combustion of hydrocarbons 4 points

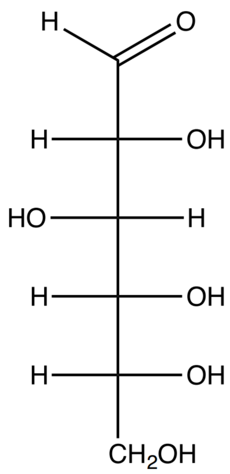
a) State the stoichiometric equation for the combustion of hexane in oxygen.

b) The negative standard combustion enthalpy (also called Heat of combustion) of hexane is $-\Delta_V H^0 = 4163.2\,\mathrm{kJ\,mol^{-1}}$. Calculate the amount of energy that a engine with an efficiency factor $\epsilon = 35\%$ can gain from $1.0\,\mathrm{l}$ hexane.

c) In model cars and dragsters one usually uses a mixture of methanol (CH_3OH) and nitromethane (CH_3NO_2). State the stoichiometric equation of combustion for a molar mixture of 1:1 between methanol and nitromethane in oxygen.

Problem 5 - Projection 3.5 points

Given below is the structure formula of D-glucose:



a) What is the name of the projection with which D-glucose is given?

b) Draw D-glucose in the skeletal formula.

c) Give for every carbon atom the hybridisation.

d) Name all chiral centers using the CIP-convention (*R*/*S*).

Problem 6 - Titration **5 points**

Oxalic acid, $H_2C_2O_4$ or $(COOH)_2$, can crystallize with zero, one or multiple molecules of water as crystallization water. The amount of crystal water shall be determined with a titration. The permanganate ion oxidizes oxalic acid in warm, acidic solutions to carbon dioxide, while forming Mn^{2+}.

0.137 g oxalic acid with zero, one or multiple molecules of water as crystallization water was weighted, transferred into an Erlenmeyer flask and dissolved in about 150 ml of water. Then 7 ml of concentrated sulfuric acid were added. The mixture was heated and titrated using a 0.02 M $KMnO_4$ solution until the rose-violet color of the permanganate was preserved. The used volume of the 0.02 M $KMnO_4$ solution was 25.5 ml.

a) Give the stoichiometric equation for the reaaction of premanganate with oxalic acid.

b) Calculate the amount of crystallization water in the oxalic acid.

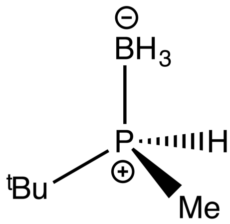
Problem 7 - Solubility product 4 points

5.0 mg aragonite (calcium carbonate) is dissolved in 1 l of water. What is the minimal amount of magnesium carbonate that has to be added to the solution such that calcium carbonate precipitates again? The solubility product of calcium carbonate is $6.0 \cdot 10^{-9}\ \mathrm{mol}^2\ \mathrm{l}^{-2}$.

PROBLEM 8 - ISOMERISM 6 POINTS

a) Draw the structural formulae of all isomers without (partial) charges (without E-/Z-isomerism) with the molecular formula C_3NH_7.

b) Draw the structural formula of the enantiomer of the the molecule given below:

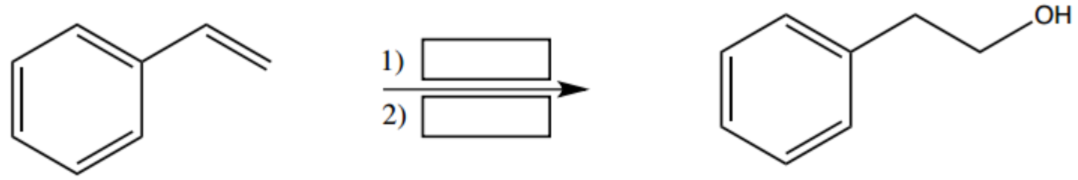


c) What is the funciton of borane in the production of functionalized phosphines?

PROBLEM 9 - ORGANIC CHEMISTRY **5 POINTS**

Complete in the following reaction the products or missing reagents (^{n}Pr = *n*-propyl).

i)



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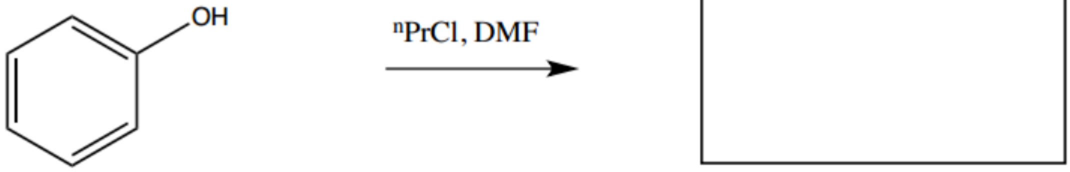

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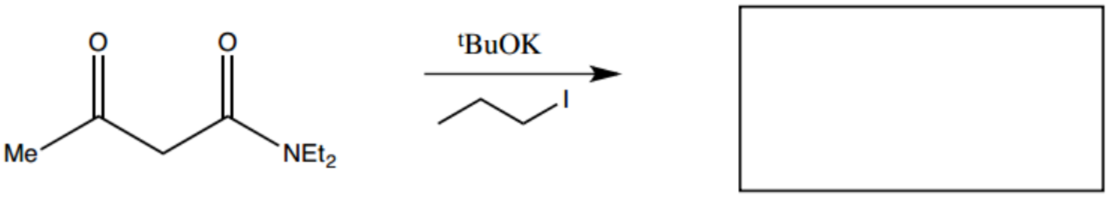

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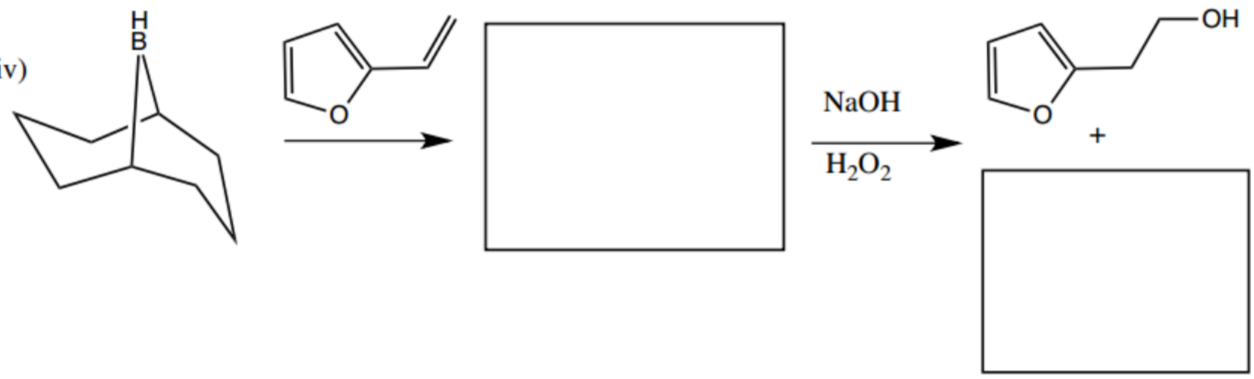
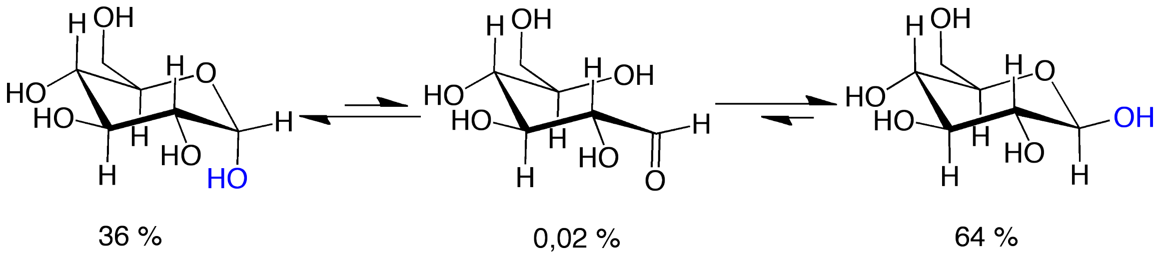


PROBLEM 10 - THE ANOMERIC EFFECTT **4 POINTS**

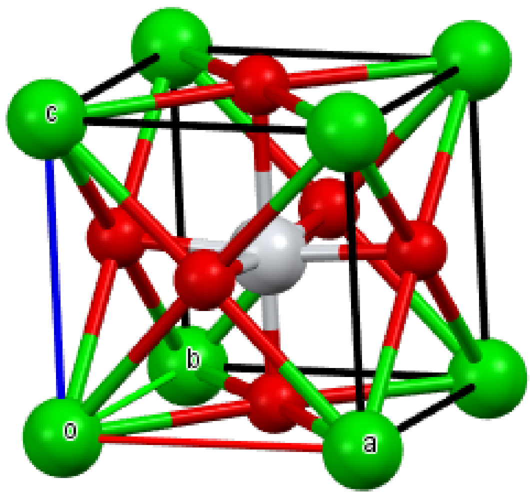
The anomeric effect denotes the effect that a heteroatom like *e.g.* oxygen, which is bound to a carbon atom of a cyclohexane ring, prefers the axial position against the sterically less hindered equatorial position, if another heteroatom is bound in the cyclohexane ring next to the aforementioned carbon atom. An example for this effect is the equilibrium between α-D-glucose and β-D-glucose.



The ratio between α-D-glucose and β-D-glucose in equilibrium at $25\ °C$ in aqueous solution is 36:74. Quantum mechanical calculations indicate that the ratio without the anomeric effect would be 11:89. Calculate the free enthalpy (also called Gibbs free energy G) at standard conditions corresponding to the anomeric effect (round the result to 0.1 kJ mol^{-1}).

Problem 11 - Crystallography 4 points

Barium titanate ($BaTiO_3$) is a mixed oxide of barium and titanium and crystallizes in the Perowskite structure. Because of its ferroelectric, dielectric and pyroelectric properties it is used as basic material for example in electronic systems and sensor technology.
Barium titanate can crystallize in different lattice types which are modifications of the Perowskite structure. The lattice parameters of a barium titanate crystal were measured as $a = 4.00\,\text{Å}$, $b = 4.00\,\text{Å}$, $c = 4.02\,\text{Å}$, $\alpha = 90°$, $\beta = 90°$ and $\gamma = 90°$. The elementary cell is given below.



a) Which crystal system and centering has this crystal?

b) Calculate the density of barium titanate.

PROBLEM 12 - INORGANIC CHEMISTRY 4 POINTS

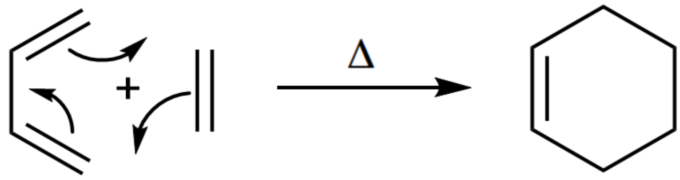
Consider the following stoichiometrically unbalanced reaction equations:

$Ca_3(PO_4)_2$ + C + SiO_2	$\longrightarrow$	**A** + ...
A + O_2 (Unterschuss)	$\longrightarrow$	**B**
A + O_2 (Überschuss)	$\longrightarrow$	P_4O_{10}
B + H_2O	$\longrightarrow$	**C**
P_4O_{10} + H_2O	$\longrightarrow$	**D**
A + H_2O + OH^-	$\longrightarrow$	**E** + **F**

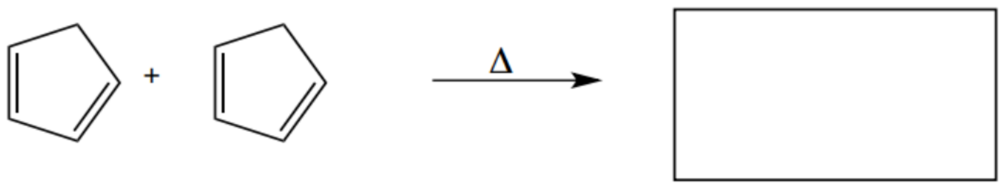
Formulate the stiochiometrically balanced reaction equation for these reactions and give the molecular formulae of the compounds **A** - **F**, which all contain phosphor. **B** has a mass fraction of phosphor of 56.3%, **F** has a mass fraction of phosphor of 47.7%.

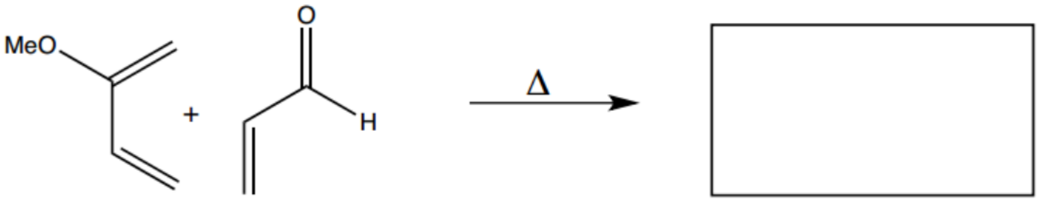
PROBLEM 13 - DIELS-ALDER REAKTION **5 POINTS**

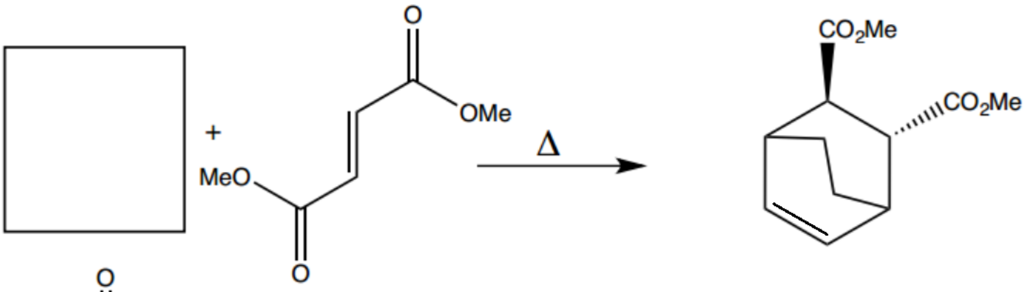
The Diels-Alder reaction is probably the most used cycloaddition reaction. There are always two reactants necessary, a diene and a dienophile. The following figure shows the prototypical example of a Diels-Alder reaction. The diene, here 1,3-butadiene is drawn as the left reactant. The dienophile, here ethene is drawn as the right reactant. Δ means heating.

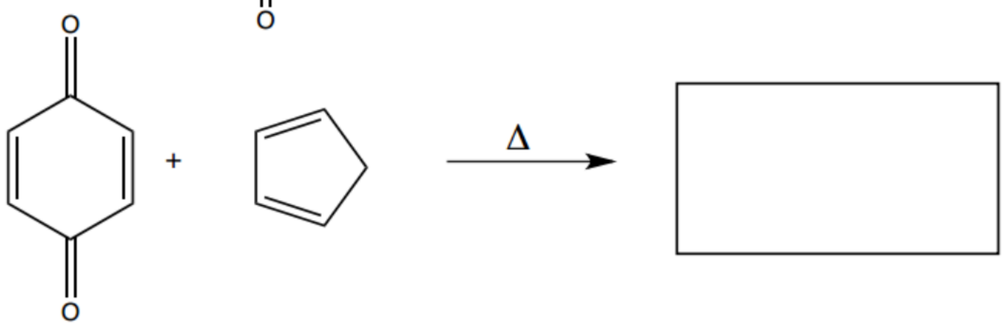


Complete in the following reactions the missing reactants and product:

i) 

ii) 

iii) 

iv) 

PROBLEM 14 - RADIOACTIVITY AND DISEASE DIAGNOSTIC 9 POINTS

a) Complete the following nuclear reactions leading to the formation of various isotopes of fluorine.

i)
$$^{18}\text{O} + {}^{1}_{1}\text{H} \rightarrow {}^{18}\text{F} + \ldots$$

ii)
$$\ldots + {}^{2}_{1}\text{D} \rightarrow {}^{18}\text{F} + {}^{4}_{2}\text{He}$$

iii)
$$^{19}\text{F} + {}^{2}_{1}\text{D} \rightarrow {}^{20}\text{F} + \ldots$$

iv)
$$^{16}\text{O} + \ldots \rightarrow {}^{18}\text{F} + {}^{1}_{1}\text{H} + n$$

b) The type of decay of unstable light nuclei depends on the ratio between neutrons and protons in the nucleus. If this ratio is bigger than for the stable isotopes, a β^- decay takes place. If it is smaller, a β^+ decay or ϵ electron capture takes place.
Determine the type of decay for the following nuclei: ^{11}C, ^{20}F, ^{17}F, ^{14}C

A derivative of glucose, 2-deoxy-2-(^{18}F)fluoro-D-glucose (FDG), is the most common radiopharmaceutical for diagnosis of cancer using positron emission tomography. The first step of FDG preparation is to produce a radionucleide fluorine-18 by nuclear reaction in a cyclotron. The next step is the radiochemical synthesis. Fluorine-18 is introduced into a D-glucose molecule by nucleophilic substitution. FDG, once injected into the patient, actively accumulates in cells of malignant tumors; this process is accompanied by decomposition of fluorine-18. This radionucleide is a β^+ emitter, meaning the nucleus emits a positron (anti-electron). This positron interacts with an electron, annihilating both particles, which can be detected. This allows determining precisely the tumor sizes and type.

c) State the differential and integrate rate law of a 1st order reaction as well as the relation between the reaction constant k and the half-life time $t_{1/2}$.

d) Calculate the yield of marked D-glucose with flourine-18 under the assumption that the initial radioactivity of the fluorine-18 sample was 600.0 MBq and the radioactivity of the obtained 2-deoxy-2-(^{18}F)fluoro-D-glucose is 528.2 MBq. The synthesis time is 3.5 minutes and the half life time of ^{18}F is $t_{1/2}(\text{F}^{18}) = 109.7$ min.

e) The biological half-life time (through the excretory organs, follows in good approximation a concentration decrease of first order) of the 2-deoxy-2-(^{18}F)fluoro-D-glucose is 120.0 minutes.
How much radioactivity (in MBq) will remain in a patient ten hours after the injection of FDG with the initial radioactivity of 450 MBq? Write down first of all the differential rate law.