Tartu University

51st CHEMISTRY OLYMPIAD

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Problems

Form 10

- 1. A and X are organic compounds. Compound A is an alcohol with the smallest number of carbon atoms, it can be obtained under high pressure in the presence of a catalyst from a toxic gas B and another gas C which is the lightest gas. Compound X is a monosaccharide which total number of atoms is equal to two times the atomic weight of carbon. Compound X is formed in plants in the process of photosynthesis. In the course of the fermentation of the aqueous solution of X there forms a compound D that belongs to the same class with A, and a gas E that causes the greenhouse effect. If all indices in the molecular formula of X were doubled and one water molecule subtracted from the obtained molecule, we would get the molecular formula of a disaccharide Y. Monosaccharides X and Z can be obtained from the compound Y. The gas E can be obtained from the oxidation of the gas B. By burning of the gas C there forms a known to all compound F which combines with the gas E under special conditions absorbing a large amount of energy and forms the monosaccharide X.
 - a) Write the names and formulas of the compounds A F and X Z.
 - b) Write the reaction equations: i) $B + C \rightarrow A$; ii) $C \rightarrow F$; iii) $B \rightarrow E$;
 - iv) E + F \rightarrow X; v) X \rightarrow D + E; vi) Y \rightarrow X + Z.
- 2. The presence of nitrogen in organic compounds is determined by the so-called Kjeldahl method, where nitrogen is turned into the ammonium ion which is then determined with acid/base titration.

Serine [$H_2N-CH(CH_2OH)-COOH$], that is an amino acid and a component of proteins, was synthesized in the laboratory. 0.500 grams of the synthesized compound with impurities was decomposed with 5 cm³ of hot concentrated sulfuric acid. ($NH_4)_2SO_4$, SO_2 , CO_2 and H_2O were formed. The reaction mixture was cooled down and 10 cm³ of 10 M KOH solution was added. Thereafter, the liquid from the reaction mixture was distilled into 50.0 cm³ of hydrochloric acid solution A. After distillation the volume of the hydrochloric acid solution was brought to 100.0 cm³ to obtain solution B. Solution B was back titrated with NaOH solution.

- a) Write the reaction equation between serine and H₂SO₄.
- b) Write the reaction equations: i) (NH₄)₂SO₄ + KOH \rightarrow product I; ii) product I $\stackrel{\sigma_1}{\longrightarrow}$ product II; iii) product II + HC1 \rightarrow .
- c) Calculate the molar concentration of the solution A, when for the titration of 10.0 cm³ of A 10.0 cm³ of 0.400% NaOH solution (1.00 g/cm³) was used.
- d) Calculate the molar concentration of the solution B, when for the back titration of 50.0 cm³ of B 12.0 cm³ of 0.400% NaOH solution (1.00 g/cm³) was used.
- e) Calculate the percentage of serine in the sample.

- 3. X and Y are nonmetallic elements of the third period. Their hydrogen compounds, A and B, have equal molecular weights. In the reaction of the compounds A and B with concentrated nitric acid, B is reduced to nitrogen monoxide and compounds C and D are formed, where the elements X and Y, respectively, have the maximum oxidation number. The compounds C and D can also be obtained by the reaction of the respective oxides E and F with water. The number of atoms in oxide E is 3.5 times larger than the number of atoms in oxide F.
 - a) Write the formulas (symbols) and names of the elements X and Y and the compounds A – F.
 - b) Write the reaction equations: i) A + HNO₃ →; ii) B + HNO₃ →; iii) E → C;
 iv) F → D.
 - c) Calculate the volume of emitted NO, when exactly 1 liter of 64.0% HNO₃ solution (1.387 g/cm³) reacts with the equivalent amount of compound B.
- 4. The energy obtained from the oxidation of glucose covers half of the energy needed by the human organism. The enthalpies of formation (ΔH_f) of glucose, carbon dioxide and water in liquid state are -1268 kJ/mol, -393.5 kJ/mol and -285.8 kJ/mol, respectively.
 - a) Write the reaction equation of the complete oxidation of glucose.
 - b) Calculate the combustion enthalpy of glucose (ΔH_c).
 - c) Calculate the mass of glucose needed by the heart per year (365 days), if the human heart beats exactly 70 times per minute and one heart beat uses 1.00 J of energy.
 - d) Calculate the number of times a human has to breath in a year, to keep working the heart only. Assume one breath to be half liters. The volume of the oxygen used is 5 volume percent of the inhaled air. At the temperature of the human body the molar volume of gas is 25.4 dm³/mol.
- 5. Concentrated acid B was poured on dark violet crystals A. As a result, a yellowish green gas C emitted, that was lead through concentrated KOH solution heated to 70–80 °C. The solution was cooled down to 1 °C. As a result 25.80 g of mixture Q of potassium chlorate and potassium chloride crystals and 65.90 g mother solution Z were formed. Upon careful heating of the mixture Q in the presence of MnO₂ its mass decreased to 22.43 grams.
 - a) Write the reaction equations; i) A + B →; ii) gas C + hot KOH →; iii) mixture Q MnO2. Ot →.
 - b) Find the mass of i) potassium chlorate and ii) potassium chloride in the mixture Q.
 - c) Find the mass of potassium chloride in solution Z, when after adding silver nitrate solution 27.35 g of precipitate was formed.
 - d) Find the mass of i) potassium chlorate that formed in the reaction, and ii) potassium chlorate in solution Z.
 - e) Find the solubility of i) potassium chloride and ii) potassium chlorate in exactly 100 grams of water at 1 °C. Assume, that the other compound does not influence the solubility of the studied compound.

- 6. Compounds A, B and C were found in the air of a chemical industry. Gas A causes the greenhouse effect. Compounds B and C are toxic and in solution with water, B gives a very strong acid while C gives a very weak acid. There are 4 atoms in the molecule of compound B and due to high vapor pressure it occurs in air as gas. In the molecule of the gas C there are 3 atoms and in compounds B and C one of the elements is the same. The compounds A, B and C, from 10.0 m³ of air, were absorbed in KOH solution. The solution was divided into three equal parts. The first part was treated with MgCl₂ solution, resulting 11.24 g of precipitate X which originated from the gas A. The second part was treated with BaCl₂ solution, resulting 119.9 g of precipitate that was a mixture of compounds Y and Z which originated from compounds A and B, respectively. The third part was treated with Pb(NO₃)₂ solution, resulting 171.2 g of precipitate that was a mixture of compounds P, Q and R which originated from compounds A, B and C, respectively.
 - a) Write the formulas and names of the compounds A, C, B; X, Y, Z and P, Q, R.
 - b) Write the reaction equations: i) A + KOH; ii) B + KOH; iii) C + KOH;
 iv) formation of X; v) formation of Y; vi) formation of Z; vii) formation of P; viii) formation of Q; ix) formation of R.
 - c) Calculate the volumes of gases i) A; ii) B and iii) C in the analyzed sample of 10.0 m³ of air, if the molar volume of the air under the conditions of the analysis was 24.0 dm³/mol.

Form 11

- 1. Mixture of gases A and B in equal volumes explodes due to flash-light, forming compound C. Gas A ignites by itself in the atmosphere of gas D also in the dark, forming compound E, that reacts with silicon dioxide in mole ratio 6: 1, giving compound F. Element G with the molar mass of 124 g/mol, burns in the atmosphere of gas B, giving binary compounds H and I. The molar mass of compound H makes 66% of the molar mass of compound I. Fine pieces of metal J ignite in the atmosphere of gas B, forming compound K, in which molecule, as also in the molecule of compound I, there are 6 atoms. Elements G and J are located in the same group of the periodic table and the number of protons in the nucleus of the element G makes 29.4% of the number of protons in the nucleus of the element J. In the reaction of the compound I with water there form compound C and a three-protonic acid L.
 - a) Write the formulas and names of compounds A L.
 - b) Write the reaction equations: i) $A + B \rightarrow$; ii) $A + D \rightarrow$; iii) $E + SiO_2 \rightarrow$; iv) $G + B \rightarrow H$; v) $G + B \rightarrow I$; vi) $J + B \rightarrow$; vii) $I + H_2O \rightarrow C + L$,
- 2. Compound X is a relatively stable salt with transparent crystals but in case of a strong stroke or by heating it decomposes with explosion, emitting gas A. This property of compound X is used in the safety pillows of the cars. The salt X is a starting material for making detonators. From the compound A

and hydrogen, compound B is obtained, in the presence of a catalyst under high pressure and temperature. By oxidation of two molecules of compound B with one molecule of sodium hypochlorite, a six-atomic compound C, NaCl and water are obtained. In the reaction of compound C with a reduced oxygen acid D of the element A there forms acid E, which's salt is compound X. Compound X can also be obtained from the reaction of compound B with sodium, resulting a salt like compound F and emition of gas G. In the reaction of compound F with laughing gas there forms the salt X. The number of atoms in compounds B, E. F and X is equal.

- a) Write the formulas and names of compounds A G and X.
- b) Write the reaction equations: i) A + H₂ →; ii) B → C; iii) C + D →; iv) B + Na →; v) F → X, vi) E + Na → X.
- 3. In living organisms, the main source of energy is the oxidation process of monosaccharides formed in the hydrolysis of starch and saccharose. This energy is used for producing the energy carrier, ATP (adenosine triphosphate). ATP is used in organisms in different processes, for example in making peptide bonds.

RCH(NH₂)COOH + RCH(NH₂)COOH = RCH(NH₂)CONHCH(R)COOH

$$\Delta$$
H⁰ = +17.0 kJ

 ΔH^0 is reaction enthalpy, ΔH^0_1 – formation enthalpy and ΔH^0_c – combustion enthalpy.

We may consider the reaction enthalpy of the transformation given above to be equal to the formation enthalpy of 1 mole of peptide bonds. ΔH (peptide bond) = +17.0 kJ/mol. Assume, that at human body temperature ΔH and ΔS are not different from their standard values.

	C ₁₂ H ₂₂ O ₁₁ (s)	O ₂	CO ₂	H ₂ O (I)
ΔH_f^0 , kJ/mol	-2222	0	-394	-286
S ⁰ , J/(mol·K)	+36 <u>0</u>	+205	+214	+7 <u>0</u>

- a) Find i) the combustion enthalpy, ΔH_c^0 , of saccharose, ii) the difference in the reaction entropy, ΔS^0 and iii) the Gibbs free energy for the reaction, ΔG , at 36.85 $^{\circ}C$.
- b) Calculate the amount of peptide bonds that an organism is able to synthesize on the account of the free energy gained from the oxidation process of one mole of saccharose. Assume, that only 40.0% of the whole free energy can be used in the mentioned processes.
- 4. Before the reaction, the density of the mixture of hydrogen and butene relative to NH₃ was 2.5. The mixture of gases constituted 2.0 moles. The mixture was heated at 320 °C in a closed 1.0 dm³ vessel in the presence of a Pt catalyst. According to the initial conditions, after the reaction, the pressure of the mixture had decreased by 20%.
 - a) Write the equation of the reaction.
 - b) Find the amount of hydrogen and butene of the initial mixture.

- c) Find the composition of the mixture in moles after the reaction and the yield percentage of the reaction.
- d) Find the equilibrium constant of the reaction.
- e) Calculate the percent of the change in the pressure of the mixture under the same conditions, if the density of the initial mixture relative to NH₃ is 3.0.
- f) Draw 6 isomers that correspond to the molecular formula of butene.
- 5. 1.6 moles of Br₂ react completely with the excess of n-butane. 37.5%mol of the reaction products is 1-bromobutane and 62.5%mol 2-bromobutane. At the given temperature the standard reaction enthalpy for this reaction was 16.8 kJ. For the reaction with the same amounts of the initial compounds, but at higher temperature, the reaction enthalpy was 17.2 kJ. The standard formation enthalpy of both bromobutanes was less than zero, however, 2-bromobutane was 4.0 kJ/mol poorer in energy compared to 1-bromobutane.
 - a) Write the reaction equations: i) n-butane → 1-bromobutane; ii) n-butane
 → 2-bromobutane.
 - b) Draw the R,S-isomers of bromobutane.
 - c) On the energy diagram, mark the location of 1-bromobutane with a solid line and 2-bromobutane with a dotted line.

E = 0
$$\Delta H_t^0$$
 (elements) = 0
E < 0 ΔH_t^0 (n-C₄H₁₀) < 0

- d) Calculate the reaction enthalpies for obtaining i) 1 mole of 1-bromobutane and ii) 1 mole of 2-bromobutane, from butane.
- e) Calculate the percentage of 1-bromo-butane among all the synthesized bromobutanes at the higher temperature.
- 6. The density of the vapors of compound X relative to air is 7.93. It does not decolorize either KMnO₄ solution or bromine water and does not change the color of an indicator solution. By burning of 2.65 g of compound X there form 3.10 liters of CO₂ and 2.28 g of water. By the treatment of X with an alkaline solution there form two molecules of tertiary alcohol A and a salt B, from which by the agency of an acid forms an acid C with a branched carbon chain. Heating of the acid C gives one molecule of carbon dioxide and one molecule of propionic acid.
 - a) Calculate the molar mass of compound X.
 - b) Find the molecular formula of compound X.
 - c) Explain and draw the graphical formulas of the compounds C, B, A and X.

Form 12

- 1. In transportation of soft and strong drinks their possible freezing must be considered, as the glass may get broken. In case of dilute solutions the decrease of the freezing temperature is linearly correlated to the molal concentration of the solution: ΔT = K_{kr}·m. Molal concentration, m, indicates the number of moles of the dissolved compound per 1 kg solvent. The cryoscopic constant of water K_{kr}(H₂O) = 1.86 K·kg/mol. Calculate, up to what temperature (°C) there is no fear of the freezing of the beer [0.988 g/cm³, %vol(alc) = 7.4], when p(alc) = 0.791 g/cm³.
- To calculate the effectiveness of the automobile engines, one has to know the value of the combustion enthalpy of the fuel at its ignition temperature (1000 K). It can be calculated from standard combustion enthalpy (ΔH_e⁰) or standard formation enthalpies (ΔH_e⁰), standard vaporizing enthalpies (ΔH_e⁰) and heat capacities C_p given in tables. Based on the Kirchhoff equation:
 ΔH^T = ΔH⁰ + ΔH_e⁰ + C_p · (T 298 K).

Consider pure n-octane as the fuel.

	n-octane (l)	O ₂ (g)	CO ₂ (g)	H ₂ O (I)
ΔH°, kJ/mol	-249.9	0	-393.5	-285.8
ΔH ⁰ , kJ/mol	41.5	_	_	. 40.7
C _n , J/(mol·K)	187.8	29.4	37.1	75.3

^{*} Heat capacity in the gaseous phase.

- a) Write the equation of the complete burning of octane.
- b) Calculate ΔH_c^0 (octane).
- c) Calculate $\Delta H_c^{1000 \text{ K}}$ (octane).
- d) Knowing, that $\Delta U = \Delta H \Delta n(g)RT$, find i) ΔU_e^0 (octane) and ii) $\Delta U_e^{1000 \text{ K}}$ (octane).
- e) Provided that in the main chain of octane there are 6 carbon atoms, draw graphically the structures of i) one R-isomer, ii) one S-isomer and iii) three isomers, where the chiral carbon is missing.
- 3. In the reaction equations, A-J are elements, with their atomic masses increasing in alphabetical order. The oxidation numbers of the elements that change in the respective reactions are indicated with Roman numerals above the elements. Elements F and J belong to the same group.

1)
$$F_3H + 6 A_8C_2\vec{E}_2 + 6 \vec{B}CG = B_6C_6\vec{E}_6 G_3H + 6 A_8C_2\vec{E} + 3 FG$$

2)
$$2 B_6 C_6 E_6 G_3 H + F_2 I + 2 FG = F_4 I + 2 B_6 C_6 E_6 G_4 H$$

3)
$$10 \text{ B}_6\text{C}_6\text{E}_6\text{G}_3\text{H} + 72 \text{ D}_3\text{G}_3^{\vee} + 24 \text{ A}_2\text{D} + 6 \text{ A}_2\text{D}_4^{\vee} = 51 \text{ D}_4^{\vee} \text{E}_6\text{G}_2 + 60 \text{ ABC} + 36 \text{ J}_2 + 5 \text{ D}_{12}\text{E}_3\text{H}_2$$

4)
$$B_6C_6E_6G_3H + A\overset{V}{C}D_3 + A_2D \rightarrow D_4\overset{VI}{E}G_2 + D_{12}\overset{VI}{E}_3H_2 + A_8C_2D_4\overset{VI}{E} + \overset{IV}{B}D_2 + \overset{II}{C}D$$

In reaction 1) compound X ($B_6C_6E_5G_3H$) is formed. In reaction 2) compound X is reduced and in reactions 3) and 4) the compound X is oxidized.

- a) Find the oxidation number of the element B in compound X according to equation 1) using an electron balancing method.
- b) Write the symbols of the elements A J.
- c) Write the reaction equations 1) -3) with the correct formulas.
- d) Find the coefficients of the reaction scheme 4) and write the respective equation with the correct formulas.
- e) Write the names of i) compound X, ii) compound $A_8C_2E_2$ and iii) the reduced form of compound X, and cations and anions formed on their complete dissociation, in case the complex ion does not decompose.
- 4. Zinc ore consisted of zinc sulfide, zinc carbonate and silicon dioxide. By heating 48.00 g of the ore, its mass was decreased by 1.32 g. 12.00 g of the ore were treated with an excess of hydrochloric acid. The emitted gases were lead through 50.09 cm³ of 0.9300 M acidic potassium permanganate solution. After absorption, when an element had formed, 32.46 cm³ of 0.5070 M solution of oxalic acid was needed for the back titration of the solution.
 - a) Write the reaction equations: i) the ore + hydrochloric acid (2 pcs);
 ii) oxidation of the emited gas with potassium permanganate;
 iii) back titration of unreacted potassium permanganate;
 iv) heating of the ore (2 pcs).
 - b) Calculate the percentage of i) zinc sulfide; ii) zinc carbonate; and silicon dioxide in the ore.
- 5. Kaur and Jasper discussed a tactical key problem of organic synthesis: how the C-C bond is formed. The target of their discussion was the formation of the compound X from toluene. Jasper proposed a scheme of synthesis that consisted of three stages. Kaur had more stages but the yield was not any lower. Both syntheses are united into one scheme whereas Jasper's scheme is to the right of toluene and Kaur's scheme is to the left.

NBS is the brominating reagent of the side chain. Compound ${\bf A}$ contains two chlorine atoms.

Compound B is an aldehyde, compound D is the Grignard's reagent. The molecular formula of X is $C_9H_8O_{\cdot}$

- a) Write i) Jasper's scheme and ii) Kaur's scheme, where compounds A-E and X are given with structural formulas.
- b) Mark the phenyl group with the symbol Ph and draw graphically the formulas of the *cis-trans* isomers of compound X.

6. Nailons are the most widely used fibrous polymers:

nailon-6

The scheme of the synthesis of nailon-6,6 is as follows:

Nailon-6,6 is formed by polycondensation of compounds **G** and **H**. From compound **C** it is possible to obtain a cyclic ether **D** which is often used as a solvent. Compound E is the initial compound of the synthetic rubber. In addition, it is known that benzene is formed by trimerization of compound **A**. 2.00 g of compound **C** solution in $10\underline{0}$ grams of water freezes at $-0.413\,^{0}$ C [K_{kr}(H₂O) = 1.86 K-kg/mol]. Compound **C** contains 53.3% of carbon and 11.2% of hydrogen. Compound **F** contains 66.7% of carbon. Ph₃PBr₂ is the brominating agent.

- a) Calculate the molecular formula of the compound C.
- b) Draw graphically the formulas of compounds A G.

Nailon-6 can be obtained by polymerization of compound J. Compound J is obtained by treating cyclohexanone with hydroxylamine, resulting the compound I ($C_6H_{11}NO$). By the treatment of the compound I in oleum there forms a lactam J ($C_6H_{11}NO$).

- c) Draw graphically the formulas of compounds I and J.
- d) Draw the graphical formulas of the products formed in the reaction of compound E with Br₂ in tetrachloro methane.

Solutions

Form 10

$$\begin{array}{lll} \text{1. a) A} - \text{CH}_3\text{OH}, \text{ methanol} & \text{F} - \text{H}_2\text{O}, \text{ water} \\ \text{B} - \text{CO}, \text{ carbon monoxide} & \text{X} - \text{C}_6\text{H}_{12}\text{O}_6, \text{ glucose} \\ \text{C} - \text{H}_2, \text{ hydrogen} & \text{Y} - \text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{ saccharose} \\ \text{D} - \text{C}_2\text{H}_5\text{OH}, \text{ ethanol} & \text{Z} - \text{C}_6\text{H}_{12}\text{O}_6, \text{ fructose} \\ \text{E} - \text{CO}_2, \text{ carbon dioxide} & \end{array}$$

p, catalyst b) i) CO + 2
$$H_2$$
 = CH₃OH ii) 2 H_2 + O_2 = 2 H_2 O iii) 2 CO + O_2 = 2 CO₂ h·v iv) 6 CO₂ + 6 H_2 O = $C_6H_{12}O_6$ + 6 O_2 ↑ regression v) $C_6H_{12}O_6$ = 2 C_2H_5 OH + 2 CO₂↑ vi) $C_{12}H_{22}O_{11}$ + H_2 O = $C_6H_{12}O_6$ + $C_6H_{12}O_6$ glucose fructose

2. a)
$$\frac{2}{3}$$
 -III IV $1(2C_3H_7O_3N) + 11H_2SO_4 = (NH_4)_2SO_4 + 6CO_2\uparrow + 10SO_2 + 14H_2O$ First, balance the number of nitrogen atoms on the left and right sides.

$$23\frac{2}{3}$$

 $2C_3 - 20e^- = 2.3\frac{231V}{C}$
VI IV
 $S + 2e^- = S$ 10

b) i)
$$(NH_4)_2SO_4 + 2 KOH = K_2SO_4 + 2 NH_3 \cdot H_2O$$

ii)
$$NH_3 \cdot H_2O = NH_3 \uparrow + H_2O$$

c) c(NaOH) =
$$\frac{1}{1 \text{ dm}^3} \cdot 1 \text{ dm}^3 \cdot \frac{1000 \text{ g}}{\text{dm}^3} \cdot 0.004 \cdot \frac{1 \text{ mol}}{40.0 \text{ g}} = 0.100 \text{ mol/dm}^3 = 0.004 \cdot \frac{1 \text{ mol}}{40.0 \text{ g}} = 0.100 \text{ mol/dm}^3 = 0.004 \cdot \frac{1 \text{ mol}}{40.0 \text{ g}} = 0.000 \cdot \frac{1 \text{ mol}}{1 \text{ mol}} = 0.000 \cdot \frac{1 \text{ mol}}{1 \text{$$

c(HCI, A) =
$$\frac{1}{1} \cdot 10.0 \,\text{cm}^3 \cdot 0.1 \,\text{M} \cdot \frac{1}{10.0 \,\text{cm}^3} = 0.100 \,\text{M}$$

d) c(HC1, B) =
$$\frac{1}{1} \cdot 12.0 \text{ cm}^3 \cdot 0.1 \text{ M} \cdot \frac{1}{50.0 \text{ cm}^3} = 0.024 \text{ M}$$

e)
$$n(serine) \Leftrightarrow n(NH_3) \Leftrightarrow n(HCI)$$

$$n(NH_3) = 0.05 \text{ dm}^3 \cdot 0.1 \text{ mol/dm}^3 + 0.1 \text{ dm}^3 \cdot 0.024 \text{ mol/dm}^3 = 0.0026 \text{ mol}$$

 $M(C_3H_7O_3N) = 105 \text{ g/mol}$

m(serine) =
$$0.0026 \text{ mol} \cdot 105 \text{ g/mol} = 0.273 \text{ g}$$

%(serine) = $\frac{0.273 \text{ g}}{0.500 \text{ g}} \cdot 100 = 54.6$

3.a) X - P. phosphorus

C - H₃PO₄, phosphoric acid

Y - S, sulfur

D - H2SO4, sulfuric acid

A ~ PH₃, phosphine, 34 g/mol

E - P₄O₁₀, tetraphosphorus decaoxide, 14 atoms in the molecule

B - H₂S, hydrogen sulfide, 34 g/mol F - SO₃, sulfur trioxide,

4 atoms in the molecule

b) i)
$$3PH_3 + 8HNO_3 = 3H_3PO_4 + 8NO + 4H_2O$$

$$N + 3e^{-} = N = 8$$

ii)
$$3H_2S + 8HNO_3 = 3H_2SO_4 + 8NO + 4H_2O$$

$$\stackrel{-11}{S} - 8e^{*} = \stackrel{V1}{S} = 3$$

 $\stackrel{V}{N} + 3e^{-} = \stackrel{N}{N} = 8$

$$N + 3e^- = N = 8$$

iii)
$$P_4O_{10} + 6H_2O = 4H_3PO_4$$

iv)
$$SO_3 + H_2O = H_2SO_4$$

 $HNO_3 \Leftrightarrow NO$ 63.0 g/mol 22.4 dm³/mol

$$V(NO) = \frac{1}{1} \cdot 1 L \cdot \frac{1000 \text{ cm}^3}{1 \text{ L}} \cdot 1.387 \text{ g/cm}^3 \cdot 0.640 \cdot \frac{1 \text{ mol}}{63.0 \text{ g}} \cdot 22.4 \text{ dm}^3/\text{mol} =$$

 $= 315.6 \text{ dm}^3 \approx 316 \text{ dm}^3$

4. a)
$$C_6H_{12}O_6 + 6 O_2 = 6 CO_2 + 6 H_2O$$

b)
$$\Delta H_c(glucose) = [6 \text{ mol} \cdot (-393.5 \text{ kJ/mol}) + 6 \text{ mol} \cdot (-285.8 \text{ kJ/mol}) -$$

-1 mol · (-1268 kJ/mol)] ·
$$\frac{1}{\text{mol}}$$
 = -2808 kJ/mol

c) Energy(heart) = 1.00 J/beat
$$\cdot$$
 365 days $\cdot \frac{24 \text{ h}}{\text{day}} \cdot \frac{60 \text{ min}}{\text{h}} \cdot 70 \text{ beats/min} =$

$$= 3.68 \cdot 10^7 J$$

m(glucose) =
$$3.68 \cdot 10^7$$
 J. $\frac{1 \text{ mol}}{2.808 \cdot 10^6}$ J. 180 g/mol = 2358 g = 2.36 kg

d) N(breaths) =
$$\frac{6}{1} \cdot 2358 \, \text{g} \cdot \frac{1 \, \text{mol}}{180 \, \text{g}} \cdot 25.4 \, \text{dm}^3 / mol \cdot \frac{1}{0.05} \cdot \frac{1}{0.5 \, \text{dm}^3} =$$

=79900 = 80000

v)
$$BaCl_2 + K_2CO_3 = BaCO_3 \downarrow + 2 \ KCl$$
vi) $BaCl_2 + K_2SO_4 = BaSO_4 \downarrow + 2 \ KCl$
vii) $Pb(NO_3)_2 + K_2CO_3 = PbCO_3 \downarrow + 2 \ KNO_3$
viii) $Pb(NO_3)_2 + K_2SO_4 = PbSO_4 \downarrow + 2 \ KNO_3$
ix) $Pb(NO_3)_2 + K_2SO_4 = PbSO_4 \downarrow + 2 \ KNO_3$
ix) $Pb(NO_3)_2 + K_2S = PbS \downarrow + 2 \ KNO_3$
c) i) V

$$CO_2 \Leftrightarrow K_2CO_3 \Leftrightarrow MgCO_3$$

$$24.0 \ dm^3/mol$$

$$V(CO_2) = \frac{1}{1} \cdot 11.24 \ g \cdot \frac{1 \ mol}{84.32 \ g} \cdot 3 \cdot 24.0 \ dm^3/mol = 0.1333 \ mol \cdot 3 \cdot 24.0 \ dm^3/mol = 9.60 \ dm^3$$
ii) $m(BaCO_3) = \frac{1}{1} \cdot 0.1333 \ mol \cdot 197.3 \ g/mol = 26.30 \ g$

$$m(BaSO_4) = 119.9 \ g - 26.30 \ g = 93.6 \ g$$

$$g3.6 \ g$$

$$VBaSO_4 \Leftrightarrow SO_3$$

$$233.4 \ g/mol = 24.0 \ dm^3/mol$$

$$V(SO_3) = \frac{1}{1} \cdot 93.6 \ g \cdot \frac{1 \ mol}{233.4 \ g} \cdot 3 \cdot 24.0 \ dm^3/mol = 0.401 \ mol \cdot 3 \cdot 24.0 \ dm^3/mol = 0.401 \ mol \cdot 3 \cdot 24.0 \ dm^3/mol = 28.9 \ dm^3$$
iii) $m(PbCO_3) = \frac{1}{1} \cdot 0.401 \ mol \cdot 303.3 \ g/mol = 121.6 \ g$

$$m(PbSO_4) = \frac{1}{1} \cdot 0.401 \ mol \cdot 303.3 \ g/mol = 121.6 \ g$$

$$m(PbS) = 171.2 \ g - 35.62 \ g - 121.6 \ g = 14.0 \ g$$

$$314.0 \ g$$

$$PbS \Leftrightarrow H_2S$$

$$239.2 \ g/mol \ 24.0 \ dm^3/mol$$

$$V(H_2S) = \frac{1}{1} \cdot 14.0 \ g \cdot \frac{1 \ mol}{239.2 \ g} \cdot 3 \cdot 24.0 \ dm^3/mol = 4.21 \ dm^3$$

Form 11

1. a)
$$A - H_2$$
, hydrogen $B - Cl_2$, chlorine $C - HCl$, hydrochloric acid $C - HCl$, hydrochloric acid $C - HCl$, hydrofluoric acid $C - HCl$, hexafluorosilicic acid $C - HCl$, phosphoric acid $C - HCl$, phosphoric acid

ii)
$$H_2 + F_2 = 2 HF$$

iii) $6 HF + SiO_2 = H_2SiF_6 + 2 H_2O$
iv) $P_4 + 6 Cl_2 = 4 PCl_3$

v)
$$P_4 + 10 Cl_2 = 4 PCl_5$$

vi) $2 Sb + 5 Cl_2 = 2 SbCl_5$
vii) $PCl_5 + 4 H_2O = 5 HCl + H_3PO_4$

2. a) A – N₂, nitrogen

B - NH₃, ammonia

C - H₂N-NH₂, hydrazine

D - HNO2, nitrous acid

E - HN₃, hydrogen azide, hydrazoic acid

F - NaNH₂, sodium amide

G - H2, hydrogen

X - NaN₃, sodium azide

b) i)
$$p_1^0 t$$

 $N_2 + 3 H_2 = 2 NH_3$

ii) $2 NH_3 + NaClO = H_2N - NH_2 + NaCl + H_2O$

iii)
$$H_2N-NH_2 + HNO_2 = HN_3 + 2 H_2O$$

iv) $2 \text{ NH}_3 + 2 \text{ Na} = 2 \text{ NaNH}_2 + \text{H}_2 \uparrow$

v)
$$NaNH_2 + N_2O = NaN_3 + H_2O$$

vi) 2 $HN_3 + 2 Na = 2 NaN_3 + H_2 \uparrow$

3. a)
$$C_{12}H_{22}O_{11} + 12 O_2 = 12 CO_2 + 11 H_2O (l)$$

i) $\Delta H^0 = \Delta H_c^0 (C_{12}H_{22}O_{11}) = 11 \text{ mol} \cdot (-286 \text{ kJ/mol}) + 12 \text{ mol} \cdot (-394 \text{ kJ/mol}) -$

- 1 mol · (-2222 kJ/mol)
$$\Rightarrow$$
 -5652 kJ · $\frac{1}{\text{mol}}$ = -5652 kJ/mol

ii)
$$\Delta S^0 = 11 \text{ mol} \cdot 70 \frac{J}{\text{K} \cdot \text{mol}} + 12 \text{ mol} \cdot 214 \frac{J}{\text{K} \cdot \text{mol}} - 12 \text{ mol} \cdot 205 \frac{J}{\text{K} \cdot \text{mol}} - 12 \text{ mol} \cdot 200 \times 10^{-3} = 10^{-3} \times 10^{-3} 10^{-3} = 10^{-3} \times 10^{-3} = 10^{-3}$$

- 1 mol · 360
$$\frac{J}{\text{K} \cdot \text{mol}}$$
 = 518 J/K

iii)
$$T = 36.85 \, ^{\circ}\text{C} + 273.15 \, ^{\circ}\text{C} = 310.00 \, \text{K}$$

$$\Delta G = \Delta G_c(C_{12}H_{22}O_{11}) = -5652 \text{ kJ} - 310 \text{ K} \cdot 0.518 \text{ kJ/K} =$$

$$-5652 \text{ kJ} - 160.58 \text{ kJ} \approx -5813 \text{ kJ} \cdot \frac{1}{mol} = -5813 \text{ kJ/mol}$$

b) n(peptide bonds) = $5813 \text{ kJ} \cdot 0.4 \cdot \frac{1 \text{ mol}}{17.0 \text{ kJ}} \approx 137 \text{ mol}$

Attention: In oxidation of saccharose energy is released, whereas in the synthesis of peptide bonds energy is absorbed.

4. a)
$$Pt_{1}^{0}t$$

$$C_{4}H_{8} + H_{2} = C_{4}H_{10}$$
56 g/mol 2 g/mol

b)
$$n(C_4H_8) \cdot 56 \text{ g/mol} + [2 \text{ mol} - n(C_4H_8)] \cdot 2 \text{ g/mol} = 2.5 \cdot 17 \text{ g/mol} \cdot 2 \text{ mol}$$

$$n(C_4H_8) = \frac{85 \text{ mol} - 4 \text{ mol}}{56 - 2} = 1.5 \text{ mol}$$

$$n(H_2) = 2 \text{ mol} - 1.5 \text{ mol} = 0.5 \text{ mol}$$

c) If y moles of hydrogen was used during the reaction, then
$$n(H_2,end)=0.5\ mol-y$$
 $n(C_4H_8,end)=1.5\ mol-y$

$$n(C_4H_{10},end) = y$$

0.5 mol - y + 1.5 mol - y + y = 2 mol (1-0.2)
y = 0.4 mol
%(yield) = 100, if all the hydrogen was used up
%(yield) = $\frac{0.4 \text{ mol}}{0.5 \text{ mol}} \cdot 100 = 80$

d)
$$K = \frac{\left[C_4 H_{1c}\right]}{\left[C_4 H_8\right] \cdot \left[H_2\right]}$$

As the volume of the reaction vessel is 1 dm³, the concentration is equal to the amount of the compound.

$$K = \frac{0.4}{0.1 \cdot 1.1} = 3.6 \text{ dm}^3/\text{mol}$$

e)
$$n'(C_4H_8) \cdot 56$$
 g/mol + [2 mol - $n'(C_4H_8)$] \cdot 2 g/mol = $3 \cdot 17$ g/mol \cdot 2 mol $n'(C_4H_8) = 1.81$ mol $n'(H_2) = 2$ mol -1.81 mol = 0.19 mol If x hydrogens is reacting, then

$$3.6 = \frac{x}{(1.81 - x) \cdot (0.19 - x)}$$

$$3.6x^2 - 8.2x - 1.238 = 0$$

$$x_1 = 0.16$$

$$x_2 = 2.11$$
, which does not fit, as n'(H₂) = 0.19 mol
$$\Sigma n(\text{end}) = (1.81 - 0.16) + (0.19 - 0.16) + 0.16 = 1.84 \text{ mol}$$

The amount and the pressure of the gaseous compound are proportional with each other.

$$\Delta p = \frac{2 \text{ mol} - 1.84 \text{ mol}}{2 \text{ mol}} \cdot 100\% = 8\%$$

c)
$$\Delta H_r^0$$
 (elements) ΔH_r^0 (1-bromobutane) ΔH_r^0 (2-bromobutane) ΔH_r^0 (n-C₄H₁₀)

d) n(1-bromobutane) = 1.6 mol · 0.375 = 0.6 mol n(2-bromobutane) = 1.6 mol - 0.6 mol = 1.0 mol 1 mol · ΔH(2-bromobutane) + 0.6 mol · [ΔH(2-bromobutane) + 4kJ/mol] = 16.8 kJ

 Δ H(2-bromobutane) = 9.0 kJ/mol Δ H(1-bromobutane) = 9.0 kJ/mol + 4.0 kJ/mol = 13.0 kJ/mol

e)
$$17.2 \text{ kJ} - 16.8 \text{ kJ} = 0.4 \text{ kJ}$$

 $\Delta n = 0.4 \text{ kJ} \cdot \frac{1 \text{ mol}}{4 \text{ kJ}} = 0.1 \text{ mol}$
 $n(1\text{-bromobutane}) = 0.6 \text{ mol} + 0.1 \text{ mol} = 0.7 \text{ mol}$
 $\% \text{mol}(1\text{-bromobutane}) = \frac{0.7 \text{ mol}}{1.6 \text{ mol}} \cdot 100 = 43.75 \approx 40$

6. a) M(X) = 29.0 g/mol 7.93 = 230 g/mol
b) n(C)
$$\Leftrightarrow$$
 n(CO₂) \Rightarrow $\frac{230 \text{ g}}{2.65 \text{ g}} \cdot 3.10 \text{ dm}^3 \cdot \frac{1 \text{ mol}}{22.4 \text{ dm}^3} = 12 \text{ mol}$
n(H) \Leftrightarrow 2n(H₂O) \Rightarrow $\frac{230 \text{ g}}{2.65 \text{ g}} \cdot 2.28 \text{ g} \cdot \frac{1 \text{ mol}}{18.0 \text{ g}} \cdot 2 = 22 \text{ mol}$
m(O)=230 g - 12 mol 12 g/mol - 22 mol 1 g/mol=230 g - 144 g - 22 g = 64 g
n(O) = 64 g $\cdot \frac{1 \text{ mol}}{16 \text{ g}} = 4 \text{ mol}$

Molecular formula of the compound X is $C_{12}H_{22}O_4$:

$$+ CO_2 = C_4H_6O_4$$
 (compound C)

Compound C was an acid with a branched chain that decarboxylated. Consequently, it can be a diacid because propionic acid was formed.

Compound B is therefore a salt of the diacid.

Compound X gave a tertiary alcohol and a salt of an acid with the aid of an alkali. The molecular formula of the anion of the salt B is $C_4H_4O_4$. The molecular formula left over from compound X is C_8H_{18} . As compound X is an ester of a diacid, the molecular formula of the alkyl group of the alcohol is C_4H_6 , which corresponds to the tert-alkyl group.

Form 12

1. It is rational to start with exactly 1 liter of beer.

$$\begin{split} & m_{ass}(beer) = 1 \text{ liter } \cdot \frac{988 \text{ g}}{1 \text{ litre}} = 988 \text{ g} \\ & V(alc) = 1 \text{ liter } \cdot 0.074 = 74 \text{ cm}^3 \\ & m_{ass}(alc) = 74 \text{ cm}^3 \cdot 0.791 \text{ g/cm}^3 = 58.53 \text{ g} \approx 59 \text{ g} \\ & m_{ass}(H_2O) = 988 \text{ g} - 59 \text{ g} = 929 \text{ g} \\ & m(alc) = 59 \text{ g} \cdot \frac{1 \text{mol}}{46 \text{ g}} \cdot \frac{1}{0.929 \text{ kg}} \\ & \Delta T = 59 \text{ g} \cdot \frac{1 \text{mol}}{46 \text{ g}} \cdot \frac{1}{0.929 \text{ kg}} \cdot 1.86 \frac{K \cdot kg}{mol} = 2.57 \text{ K} \approx 2.6 \text{ K} \end{split}$$

Note: Beer also contains other components, allowing to round ΔT to the higher value.

$$T = 0 \, ^{\circ}C - \Delta T = -2.6 \, ^{\circ}C$$

2. a)
$$C_8H_{18}(v) + 12.5O_2(g) = 8CO_2(g) + 9H_2O(v)$$

b) $\Delta H_c^0(C_8H_{18}) = [8\cdot(-393.5 \text{ kJ}) + 9\cdot(-285.8 \text{ kJ}) - (-249.9 \text{ kJ})] \cdot \frac{1}{\text{mol}} =$
= -5470.3 kJ/mol

c) 1000 K
$$-298$$
 K = 702 K
 $\Delta H_c^{1000 \text{ K}}$ (C₈H₁₈) = -5470.3 kJ/mol + (9·40.7) kJ/mol -- 41.5 kJ/mol +
+702 · (0.0753·9 + 0.0371·8-0.0294·12.5-0.1878) kJ/mol =
= -4851.2 kJ/mol

d) i)
$$\Delta U_c^0$$
 (octane) = -5470.3 kJ/mol - (8-12.5) mol·8.314 $\frac{J}{K \cdot mol}$ ·298 K · $\frac{1kJ}{1000J}$ = -5459.2 kJ/mol ii) $\Delta U_c^{1000 \text{ K}}$ (octane) = -4851.2 kJ/mol - (17-13.5)·8.314 $\frac{J}{K \cdot mol}$ ·1000 K· $\frac{1kJ}{1000J}$ = -4880.3 kJ/mol e) ii)

:2

3. a)
$$6 \cdot 2 \cdot (-1)$$
 12·(-11)
E - 12e- = E
6·II 6·z
B + 12e' = B
 $z = \frac{12+12}{6} = 4$
b) A B C D E F G H I J
H C N O S CI K Fe Sn I

- c) 1) FeCl₃ + 6(NH₄)₂S₂ + 6KCN = K₃[Fe(SCN)₆] + 6(NH₄)₂S + 3KCl 2) 2K₃[Fe(SCN)₆] + SnCl₂ + 2KCl = SnCl₄ + 2K₄[Fe(SCN)₆] 3) 10 K₃[Fe(SCN)₆] + 72KlO₃ + 24H₂O + 6H₂SO₄ = 51K₂SO₄ + 60HCN+ + 36l₂ + 5Fe₂(SO₄)₃
- d) $2 ext{ K}_3[Fe(SCN)_8] + 32HNO_3 + 8H_2O = 3K_2SO_4 + 1Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 12CO_2 + 32NO_4 + 6(NH_4)_2SO_4 + 12CO_2 + 32NO_4 + 12CO_4 + 12CO_4 + 32NO_4 + 12CO_5 + 32NO_4 + 12CO_5 + 32NO_4 + 12CO_5 + 32NO_5 + 32N$
- e) i) potassium hexathiocyanatoferrate (III) $K_3[Fe(SCN)_6] \rightarrow -3K^* + [Fe(SCN)_6]^3$:
 ii) ammonium disulfide $(NH_4)_2S_2 \rightarrow -2NH_4^+ + S_2^2$.
 - iii) potassium hexathiocyanatoferrate (II) K₄[Fe(SCN)₆] -- 4K⁺ + [Fe(SCN)₆]⁴⁻

4. a) i)
$$ZnS + 2HCI = ZnCI_2 + H_2S \uparrow$$
 $ZnCO_3 + 2HCI = ZnCI_2 + H_2O + CO_2 \uparrow$
ii) $2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$
iii) $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$
iv) $ZnCO_3 = ZnO + CO_2$
 $ZnO + SiO_2 = ZnSiO_3$
b) i) $n(ZnS) \Leftrightarrow n(H_2S) \Leftrightarrow \frac{5}{2}n(KMnO_4, before) - n(H_2C_2O_4)$
 $n(ZnS) = \frac{5}{2} \cdot 0.9300 \text{ mol/dm}^3 \cdot 0.05009 \text{ dm}^3 - 0.5070 \text{ mol/dm}^3 \cdot 0.03246 \text{ dm}^3 = 0.1000 \text{ mol}$
% $(ZnS) = 0.1000 \text{ mol} \cdot 97.46 \text{ g/mol} \cdot \frac{1}{12.00 \text{ g}} \cdot 100 = 81.21$
ii) $n(ZnCO_3) \Leftrightarrow n(CO_2)$
 $n(ZnCO_3) = 1.32 \text{ g} \cdot \frac{1 \text{ mol}}{44.01 \text{ g}} \cdot = 0.0300 \text{ mol}$
% $(ZnCO_3) = 0.0300 \text{ mol} \cdot 125.4 \text{ g/mol} \cdot \frac{1}{48.00 \text{ g}} \cdot 100 = 7.84$

iii)
$$%(SiO_2) = 100 - 7.84 - 81.21 = 10.95$$

Ε

X

Kaur's scheme

trans-isomer

cis-isomer

6. a) 0.413 K = 1.86 K·kg/mol · 2 g/M(compound C) · 1/0.1 kg M(compound C) = 1.86 K·kg/mol · 2 g · 1/0.1 kg · 1/0.413 K = 90.1 g/mol $n(C) = 90.1 \text{ g} \cdot 0.533 \cdot \frac{1 \text{mol}}{12 \text{ g}} = 4 \text{ mol}$ $n(H) = 90.1 \text{ g} \cdot 0.112 \cdot \frac{1 \text{mol}}{1 \text{ g}} = 10 \text{ mol}$

 $n(O) = 90.1 \text{ g} \cdot (1 - 0.533 - 0.112) \cdot \frac{1\text{mol}}{16 \text{ g}} = 2 \text{ mol}$

Compound C is C₄H₁₀O₂.