The 2<sup>nd</sup> Abu Rayhan al-Biruni International Chemistry Olympiad

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# ABU RAYHAN BIRUNI INTERNATIONAL CHEMISTRY OLYMPIAD

# Solutions to preparatory problems

Ministry of Preschool and School Education of the Republic of Uzbekistan



Science Olympiad Center



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(International Mendeleev Chemistry Olympiad, 2024, the 1<sup>st</sup> exam, Problem 2)

**1.**  $C_XH_Y$ , giving precipitate with the ammonia solution of silver oxide is terminal alkyne. Since **B** contains 5 carbon atoms, the alkyne can be acetylene, propyne, or butyne-1. If  $C_XH_Y$  is acetylene, then **A** must contain 3 carbon atoms, i.e., it is acetone (propanal would give a silver mirror reaction). The variants with propyne and butyne are also invalid, since otherwise **A** would be an aldehyde (ethanal or methanal, respectively). **II** is 2-methylbuta- 1,3-diene (isoprene).



**2.** The addition of acetylene to acetone occurs under conditions of base catalysis in the presence of KOH, which generates a reactive acetylenide anion. LDA, which is a very strong base, is used in stoichiometric rather than catalytic amounts; the basicity of triethylamine is insufficient to deprotonate acetylene.

3. Let's denote I as an isoprene oligomer, i.e. as  $(C_5H_8)_n$ .  $M = (12 \cdot 5 + 8) \cdot n = 272$ ; n = 4 (diterpene),  $I - C_{20}H_{32}$ .

4.  $n(\mathbf{I}) = m/M = 16.32/272 = 0.06 \text{ mol};$   $n(\mathbf{H}_2) = pV/(RT) = 2.3 \cdot 2.764 / (0.082 \cdot 323) =$ 

= 0.24 mol;  $n(H_2)/n(I) = 0.24 / 0.06 = 4$ , i.e. one molecule of cembrene contains 4 double bonds. On the other hand, its degree of unsaturation  $(n_{ring} + n_{C=C})$  equals 5 from the molecular formula of **I**; so  $n_{ring}$  equals 1.

5. In the spectrum of trans-4-octene, the signal with  $\delta > 5$  ppm with the lowest intensity corresponds to 2 olefinic protons (*a*). The signals *b* and *c* have equal intensities and belong to the protons of allylic and homoallylic positions, respectively (the chemical shift of the signal *b* is greater due to the fact that the acceptor C=C bond is located closer to these protons). The most intense signal is due to the protons of two CH<sub>3</sub> groups.



Dihydrocembrene is obtained from cembrene by the addition of two H atoms, i.e. it has the molecular formula of  $C_{20}H_{34}$ . It can be seen that the total intensity of the signals in both spectra (the height of the jumps in the integral curve) coincides with the total number of protons in each of the compounds: 16 protons for *trans*-4-octene and 34 protons for **III**. This means that the number of H

atoms in each signal is equal to the jump height of the curve. The signal located about 5 ppm is due to the olefinic protons in *trans*-4-octene; the total intensity of this range for **III** is 4. So  $n_{\rm H}$ - $sp^2 = 4$ H;  $n_{\rm H}$ - $sp^3 = 34$ H - 4H = 30H.

6. Let us consider the structures of 2-isopropyl-5-oxohexanoic and 2-methylpentanedioic acids.



The fragments of these compounds contribute in total three olefinic protons in the case of **III** (since the ketone group is formed during ozonolysis from -C=, and the carboxyl one from -CH=). In the previous question, we found that the molecule of **III** has four olefinic protons, which means that there is one olefinic H atom for **X**. Since there are no carbon-containing products but those indicated in the task text, all the C=C double bonds are found in the ring. Then **X** is a



ketoacid containing 20 - 9 - 6 = 5 C atoms with the molecular formula of C<sub>5</sub>H<sub>8</sub>O<sub>3</sub>. One can propose five ketoacids of this composition:

The second and fifth acids are unstable  $\beta$ -oxoacids, spontaneously undergoing decarboxylation, therefore they cannot be obtained as a result of oxidative ozonolysis. Of the remaining options, the first and fourth ketoacids contain a ketone group in the  $\alpha$ -position to the carboxyl one; such fragment is formed as a result of ozonolysis of the conjugated diene fragment, but dihydrocembrene **III** cannot contain it, since it is obtained by the reduction of 1,3-dienes with hydrogen from Li/NH<sub>3</sub>. Then 4-oxopentanoic acid (levulinic) is the only option left for **X**.

7. The carbon skeleton is not destroyed during the reduction of **I** to **III**. This means that the ring size in cembrene is equal to the sum of the distances (expressed in the number of atoms) between the carbon atoms bonded to oxygen for all three ozonolysis products of **III**. It equals to: 5 [2-isopropyl-5-oxocaproic acid] + 5 [2-methylglutaric acid] + 4 [levulinic acid] = 14.

(International Mendeleev Chemistry Olympiad, 2006, the  $2^{nd}$  exam, Inorganic Chemistry, Problem 3) **1.** Since  $\omega(C) : \omega(H) = n$ , one can find *n* from the equation:  $\frac{12n}{14n-4} : \frac{2n-4}{14n-4} = n$ ; thus, n = 8. Therefore, the hydrocarbon is  $C_8H_{12}$ . From the <sup>1</sup>H NMR spectrum, it follows that  $C_8H_{12}$  has two kinds of protons in a ratio of 2 : 1; eight protons are connected to saturated carbon atoms ( $\delta = 2.36$  ppm) and 4 are olefinic hydrogens ( $\delta = 5.57$  ppm). These NMR data (two signals; 12 protons) and the method of synthesis (cyclization of alkadiene) indicate that the cyclic hydrocarbon is symmetric. This is *cis*, *cis*-cyclooctadiene-1,5 having chair and boat conformations:



**2.** From the scheme (1), **A** contains  $b\mathbf{X}$ ,  $b\mathbf{C}_{n}\mathbf{H}_{2n-4}$  and  $3b + 2b - 2b^{2} = 5b - 2b^{2}$  Cl atoms, thus the formula is  $b\mathbf{X}$   $b\mathbf{C}_{8}\mathbf{H}_{12}$ ·( $5b - 2b^{2}$ )Cl. Then, from the expression:

$$\omega(\mathbf{X}) = \frac{b \cdot A(\mathbf{X})}{b \cdot A(\mathbf{X}) + b \cdot 108.2 + (5b - 2b^2) \cdot 35.45} = 0.4173$$

it follows that  $A(\mathbf{X}) = 204.4 - 50.77b$ . At  $b = 2 A(\mathbf{X}) = 204.4 - 50.77 \cdot 2 = 102.9$  g/mol, therefore **X** is rhodium (Rh). At  $b = 3 A(\mathbf{X}) = 204.4 - 50.77 \cdot 3 = 52.09$  g/mol; *d*-metal is Cr, however, this solution is not valid because [Cr(C<sub>8</sub>H<sub>12</sub>)Cl]<sub>2</sub> would be paramagnetic.

From scheme (2), for b = 2 the formula of **B** is  $\mathbf{Z} \cdot 2C_8 H_{12} \cdot \mathbf{Y} \cdot 3Cl$ . Since  $\omega(\mathbf{C}) = \omega(\mathbf{Z})$ , then:

$$\frac{16\cdot 12.01}{M(\boldsymbol{B})} = \frac{A(\boldsymbol{Z})}{M(\boldsymbol{B})},$$

the atomic weight  $A(\mathbf{Z}) = 192.2$  g/mol; therefore, **Z** is *d*-metal iridium (Ir).

**3.** Since in **B**  $\omega(\mathbf{Z}) = 1.619 \ \omega(\mathbf{Y})$ , then  $A(\mathbf{Z}) = 1.619 \ A(\mathbf{Y})$ .  $A(\mathbf{Y}) = \frac{A(\mathbf{Z})}{1.619} = \frac{192.2}{1.619} = 118.7 \frac{g}{mol}$ ;

**Y** is Sn. SnCl<sub>2</sub> acts as reductant in the reaction (1). It acts as reductant and anionic ligand (SnCl<sub>3</sub><sup>-</sup>) in the reaction (2).

**4.** The formula of **A** is  $[Rh(C_8H_{12})Cl]_2$ , CN(Rh) = 4 ( $C_8H_{12}$  and Cl are bidentate and monodentate ligands respectively); oxidation number is +1.

The formula of **B** is  $[Ir(C_8H_{12})_2SnCl_3]$ , CN(Ir) = 5  $(SnCl_3^-$  is a monodentate ligand); oxidation number is +1; if the ligand is bidentate,  $C_8H_{12}$  has the following structure:



**5.** Rhodium atom possesses the  $d^2s$  hybridization in RhCl<sub>3</sub>; in the complex **A** it has  $dsp^2$  hybridization. In Na<sub>2</sub>IrCl<sub>6</sub>, iridium has  $d^2sp^3$  hybridization; in the complex **B** it is  $dsp^3$ .

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**6.** In **A** the polyhedron is a distorted square, in **B** it is a square pyramid.



 $A(C_{2V})$  distorted square

**B** (C<sub>4V</sub>) square pyramid

(International Mendeleev Chemistry Olympiad, 2008, the 2<sup>nd</sup> exam, Inorganic Chemistry, Problem 2)

**1.** According to the problem statement, **A** contains metal **X** in two different oxidation states, so the recognition of **X** starting from **A** is not the easiest way. Calculations, taking compositions of **F** and **G** as a starting point, look more reasonable, since the latter one is a gas containing **X** in a definite oxidation state. **F** and **G** are binary compounds. Besides, they are fluorides of the element under investigation, since the former is a result of the reaction between **E** and hydrogen fluoride, and the latter is a product of the interaction of **F** with fluorine. Let M is a molar weight of **X**, then one can construct the following ratio:  $\frac{1}{M+19n} = \frac{0.891}{M+19m}$ , where n > m. Recasting the ratio leads to:  $0.1223 \cdot M = 19 \cdot (n - 1.1223 \cdot m)$ , i.e.  $M = 155.31 \cdot (n - 1.1223 \cdot m)$  g/mol. Let us fill the table:

n / m	2	3	4	5	6
1	136.32 (Ba)	291.63	446.94	602.25	757.56
2		— 117.32 (In, Sn) 272.63 427.94		427.94	583.25
3	_		98.33 (Tc)	253.64	408.95
4				79.33 (Se)	234.64 (U)
5					60.34 (Ni, Co)

Either redox transitions between fluorides with corresponding oxidation numbers of elements: Ba, In, Sn, Tc, Se do not demand the use of fluorine, or the products of such transformations are not gases. In cases of Ni or Co, oxidation numbers of +5 and +6 can not be reached. Thus,  $\mathbf{X} = {}^{235}$ U appears to be a reasonable choice. Below is the table with the results of calculations for the case when 1 g of **G** gives 0.892 g of **F**.

n / m	2	3	3 4		6
1	137.93 (Ba, Ce)	294.86 451.79		608.72	765.65
2		118.92 (Sb, Sn)	275.85	432.78	589.71
3			99.92 (Tc, Ru)	256.85	413.78
4				80.91 (Se, Br)	237.84 (U)
5					61.91 (Co, Cu)

All notes made above are still valid. Reasonable choice here is  $\mathbf{X} = {}^{238}$ U. Therefore, metal **X** is uranium, **F** is UF<sub>4</sub>, **G** is UF<sub>6</sub>. Calculation of the composition of oxide **A**, stipulating that one of the two oxidation numbers is +6, gives:

$$n(U): n(O) = \frac{84.4\%}{238}: \frac{15.2\%}{16} = 0.3563: 0.950 = 1: 2.6663 \approx 3: 8$$
, then A is U<sub>3</sub>O<sub>8</sub>.

To obtain a solution of **B** from **A**, oxidant NaClO<sub>3</sub> is used, whereas the transformations of **G** to **C** and

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**B** to **C** are not associated with redox processes, since no redox agents are applied. The same color of **B** and **C** is an indirect support for this statement. As far as the maximum oxidation number for uranium is +6, one can conclude that the oxidation number of uranium in **B** is +6, too. The composition of the anion of **B** acid is indicative of charge compensation for the central atom with 3 anions  $SO_4^{2-}$  in the complex anion. This means that the cation has to contain one uranium atom and two oxygen atoms, i.e. it is uranyl  $UO_2^{2+}$  Since uranium does not form bridged cations in solution, consideration of ions  $U_xO_y^{2+}$  with x > 1 is to be excluded. **B** is H<sub>4</sub>[(UO<sub>2</sub>)(SO<sub>4</sub>)<sub>3</sub>]. Considering the reaction leading to salt **C**, one has to conclude that nitrogen is present in the salt in the form of NH<sub>4</sub><sup>+</sup>, as far as any other cations are absent. What kind of anion does **C** contain? The anion seems to be  $U_pO_q^{(2q-6p)-}$ ; then, according to the problem statement, p = 2q - 6p, or 7p = 2q. The simplest solution is p = 2, q = 7, and, consequently, the composition of **C** is  $(NH_4)_2U_2O_7$ . Since **D** is a binary compound, it is an oxide. Thermal decomposition of  $(NH_4)_2U_2O_7$  is not coupled with a variation of the oxidation numbers of elements, as it is evidenced by stable yellow color of the reagent and the product. **D** is UO<sub>3</sub>. Treatment of **E** with HF leading to UF<sub>4</sub> is not a redox reaction, therefore, **E** is UO<sub>2</sub>.

$$\begin{split} 3U_{3}O_{8} + NaClO_{3} + 28H_{2}SO_{4} &\rightarrow 9H_{4}[(UO_{2})(SO_{4})_{3}] + HCl\uparrow + NaHSO_{4} + 9H_{2}O \text{ or} \\ 5U_{3}O_{8} + 2NaClO_{3} + 47H_{2}SO_{4} &\rightarrow 15H_{4}[(UO_{2})(SO_{4})_{3}] + Cl_{2}\uparrow + 2NaHSO_{4} + 16H_{2}O \text{ or} \\ U_{3}O_{8} + 2NaClO_{3} + 11H_{2}SO_{4} &\rightarrow 3H_{4}[(UO_{2})(SO_{4})_{3}] + 2ClO_{2}\uparrow + 2NaHSO_{4} + 4H_{2}O. \\ 2H_{4}[(UO_{2})(SO_{4})_{3}] + 14NH_{3} \cdot H_{2}O \rightarrow (NH_{4})_{2}U_{2}O_{7}\downarrow + 6(NH_{4})_{2}SO_{4} + 11H_{2}O \\ (NH_{4})_{2}U_{2}O_{7} \rightarrow 2UO_{3} + 2NH_{3}\uparrow + H_{2}O\uparrow UO_{3} + H_{2} \rightarrow UO_{2} + H_{2}O \\ UO_{2} + 4HF \rightarrow UF_{4} + 2H_{2}O & UF_{4} + F_{2} \rightarrow UF_{6} \\ UF_{4} + 2Mg \rightarrow U + 2MgF_{2} & UF_{6} + H_{2} \rightarrow UF_{4} + 2HF \\ 2UF_{6} + 14NH_{4}HCO_{3} \rightarrow (NH_{4})_{2}U_{2}O_{7}\downarrow + 12NH_{4}F + 14CO_{2}\uparrow + 7H_{2}O \end{split}$$

**2.** Nuclear power industry is interested in isotope  $^{235}$ U that participates in chain fission reaction. In the course of centrifugation UF<sub>6</sub> is enriched with the lighter isotope.

**3.** The complexes cannot contain different ligands, otherwise the condition of equivalence of carbon atoms would be broken. The composition can be written as  $UL_c$  (L is a cyclic ligand due to the condition above, *c* is a natural number). The charge of the ligand can be deduced from the rule for aromatics (the number of  $\pi$ -electrons = 4n + 2, n = 0, 1, 2, ...).

		$UC_{20}H_{20}$	UC <sub>16</sub> H <sub>16</sub>		
	L	Oxidation number	L	Oxidation number	
<i>c</i> = 1	$C_{20}H_{20}^{2-}$	+2	$C_{16}H_{16}^{2-}$	+2	
<i>c</i> = 2	$C_{10}H_{10}$	0	$C_8 H_8^{2-}$	+4	

	$C_{10}H_{10}^{4-}$	+8		
<i>c</i> = 3	-	-	-	-
<i>c</i> = 4	$C_5H_5^-$	+4	$C_4 H_4^{2-}$	+8

The only solution is complexes  $U(C_5H_5)_4$  and  $U(C_8H_8)_2$ :



J(C	5H	5)4	



 $U(C_8H_8)_2$ 

#### (The VI All-Russian Internet Olympiad "Nanotechnology - a breakthrough into the future", 2012)

1. Of the canonical amino acids, glycine (Mg = 75.07 g/mol) and tryptophan (Mg = 204.23 g/mol) have the lowest and highest molecular weights, respectively. The calculation of the minimum and maximum possible number of amino acid residues in an arbitrary peptide can be carried out based on an easily deducible formula:

$$n \cdot M_{acid} - (n-1) \cdot M_{water} = M_{pep} \Rightarrow n = \frac{M_{pep} - M_{water}}{M_{acid} - M_{water}}$$

Substituting the reference values, we obtain that the number of amino acid residues in an oligopeptide ranges from 9 (a nonapeptide based on tryptophan, but not exclusively from it - at least one residue must be from another, less massive amino acid) to 28 (polyglycine). Carefully round up the results of such calculations. For example, in this example, for tryptophan, the mathematically correct answer is 8.58, and the chemical answer is 9. However, it should be understood that for such estimates, the accuracy given by the number of significant digits in the molecular weight of the peptide is clearly excessive - the same conclusions are obtained when using masses rounded to а whole. Also note the fact that for the synthesis of a cyclic peptide from n amino acid molecules, the number of water molecules formed simultaneously is n-1. Ignoring this fact leads to incorrect calculations and conclusions.

2. The molecular weights of these three amino acids are: alanine -89.09 g/mol, glutamic acid -147.13 g/mol and lysine -146.19 g/mol. It can be seen that the molecular weights of glutamine and lysine are close enough, so for further calculations we can make a reasonable assumption that X-II is formed by two amino acids with molecular weights of 89 (M1) and 146.6 g/mol (M2). Then the equation (n is the number of alanine residues) is valid:

$$M_{pep} + 15 \cdot M_{water} = n \cdot M_1 + (16 \cdot n) \cdot M_2$$

The solution of this equation leads to n = 8. Further determination of the amount of glutamate and lysine residues is based on the application of an equation similar in form (m is the number of glutamic acid residues):

$$147,13 \cdot m + 146,19 \cdot (8 \cdot m) = 1173,28 \Rightarrow m = 4$$

Thus, the gross composition of the desired peptide is  $A_8E_4K_4$ . If you do everything right, you will certainly understand that simplifying the situation using logical constructions is extremely useful when choosing a strategy for solving such problems. **3.** Note that for all three peptides, the number of hydrolysis products is four, and no free amino acids are formed during trypsin treatment (this is a very important observation based on simple mathematical calculations according to the table). Accordingly, lysine residues cannot be *N*-terminal: if lysine is at the *N*-end, a free amino acid would be formed during enzymatic hydrolysis; however, they must be at the *C*-end of the peptides: otherwise, the number of hydrolysis products of any of the three peptides would be five. The general rule is that if you have n points of fragmentation of a linear object, then the number of pieces formed is n+1.

Since the desired biomolecules lack peptide bonds formed simultaneously by glutamic acid and lysine, only two alanine patterns are possible:

 $A_A A_A A_A A_A (1)$  or  $A_A A_A A_A A_A (2)$ .

In the case of option (1), peptides containing an odd number of amino acid residues would be formed during hydrolysis, which contradicts the condition. Therefore, option (2) is suitable, which, taking into account the previous conclusions, transforms into the following sequence:

#### A\_A\_A\_A\_A\_AK (3).

The only possible formula for tetrapeptide, the product of X-I hydrolysis, is AEAK [note the terminal fragment of the molecule (3)]. From here it is easy to see that a single formula can correspond to the X-I peptide:

#### AEAK<u>AEAK</u>AEAK<u>AEAK</u>

Based on such considerations, it is not difficult to determine the structural formula of the decapeptide formed from X-IV – AEAEAEAEAK. Based on formula (3), there are four possible amino acid sequences X-IV, which are obtained by sequentially moving AK fragments from the end of the bipolymer to its beginning:

AEAEAEAEAKAKAKAK (IV-1) AKAEAEAEAEAKAKAK (IV-2) AKAKAEAEAEAEAKAK (IV-3) AKAKAKAEAEAEAEAK (IV-4)

Let's try to determine the logic of the Roman numerals I and IV in the designation of peptides. The location of the alanine residues is rigidly fixed, so we need to consider ways of possible interposition of the other two amino acids. The only reasonable option is that Roman numerals reflect the number of identical amino acid residues that are inextricably following each other (when alanins are mentally overlooked). Simply put, in peptide **X-I**, the lysine and glutamic acid residues follow alternately (highlighted in underscores and bold, respectively):

#### AEAKAEAKAEAKAEAK

According to this logic, formula IV-1 is suitable for peptide **X-IV**, where lysine and glutamate residues are grouped into four groups:

#### ΑΕΑΕΑΕΑΚΑΚΑΚΑΚ

The composition of the hydrolysis products of compound **X-II** uniquely includes two hexapeptides AEAEAK and two dipeptides AK. In this case, the residues of lysines and glutamates are grouped in two, hence the only possible formula **X-II** is as follows:

#### ΑΕΑΕΑΚΑΚΑΕΑΕΑΚΑΚ

4. In this case, the formation of supramolecular structures is explained by the fact that on one side of the plane of the peptide aggregate there will be only hydrophobic groups (methyl groups of alanine), on the other - hydrophilic groups with a certain alternation of positive and negative charges on them. In an aqueous solution, the molecules of these peptides are capable of forming aggregates due to both hydrophobic and electrostatic interactions. In this way, long peptide fibers are formed, which intertwine with each other during growth and form a hydrophilic matrix containing up to 99.9% water and representing an ideal environment for the correct architectonics of stem cell growth. The main idea in solving this issue is the fact that synthetic polypeptides are built by researchers on the basis of a two-level alternation of amino acid residues: alanins follow each other (the first level), lysine and glutamic acid containing functional groups charged under physiological conditions in the side chain, one at a time, in pairs or in fours (the second level of construction). It is clear that the authors of the work tried to find the most optimal functional molecule due to differences in the alternation of amino acids charged differently at physiological pH values. The function of an amino acid polymer is directly determined by the secondary and tertiary structure of its aggregates, which are formed by hydrophobic interactions of methyl groups, electrostatic interactions between NH<sub>3+</sub> (lysine) and COO- (glutamate), as well as intermolecular hydrogen bonds similar to those that form the classical folded  $\beta$ -structure of polypeptide chains.

(The VI All-Russian Internet Olympiad "Nanotechnology - a breakthrough into the future", 2012)

**1.** Based on the molar ratio of hydrolysis products – free amino acids, it can be assumed that peptide **A** should contain 7n amino acid residues (n $\in$ N). However, even in the case of n=2, the average molecular weight of the amino acids forming the peptide will be:

$$M(average) = \frac{572,67 + 13 \cdot 18,01}{14} = 57,62 \ g/mol,$$

which is much less than the molecular weight of glycine, the simplest amino acid. Therefore, n=1, and **A** is a heptapeptide.

2. The formula of peptide A can be represented as  $XY_6$ . Let's try to calculate the average molecular weight of amino acids in A again:

$$M(average) = \frac{572,67 + 6 \cdot 18,01}{7} = 97,25 \ g/mol$$

Of the canonical amino acids, only two have a lower molecular weight value than 97.25 g/mol – glycine (75.07 g/mol) and alanine (89.09 g/mol). Going through the four options presented in the table below leads to the only possible answer – peptide **A** has the formula LysAla<sub>6</sub>.

voriont	molecular weight of the second amino	name of the second amine acid		
variant	acid, g/mol			
$\mathbf{X} - \mathbf{Gly}$	100,94	-		
Y – Gly	230,31	-		
$\mathbf{X} - Ala$	98,61	-		
Y – Ala	146,19	lysine (Lys)		

In most of these tasks, it will not be possible to completely avoid going through the options, so the best approach to solving it is to make several assessments and significantly narrow down the range of options to consider. At the same time, determining the average molecular weight of the monomers forming the biopolymer serves as a good strategy in optimizing the search – the main emphasis is on the fact that there will be a limited number of elements below or above the value obtained (and these areas must be filled, since we are dealing with the arithmetic mean).

**3.** It is easy to find out from the reference literature that the enzyme trypsin hydrolyzes the bonds formed by the carboxyl group of lysine. Due to the fact that the treatment of peptide **B** with trypsin does not lead to any results, it can be concluded that the lysine residue in this case is the *C*-terminal, and the formula of oligopeptide **B** can be represented as:

Since the peptide contains the maximum number of peptide bonds linking the residues of the amino acid  $\mathbf{Y}$  (alanine) to each other, the lysine residue should be only terminal. It cannot be *C*-terminal (peptide **B** has such a structure), which means that lysine is located at the N-terminus of oligopeptide **A**:

#### Lys-Ala-Ala-Ala-Ala-Ala

**4.** Let's remember that surfactants are compounds with an amphiphilic structure, that is, their molecules contain a polar part or a hydrophilic component and a nonpolar part or a hydrophobic component.

For the Lys-Ala-Ala-Ala-Ala-Ala-Ala peptide, the total charge of the molecule will change at different pH values due to the processes of (de-)protonation. At pH 2, the carboxyl group of *C*-terminal alanine (pKa~2.5) is mostly in protonated form, thereby giving the peptide a pronounced hydrophilic head (total charge +2) and a hydrophobic tail. In other words, at pH 2, optimal conditions are created for the formation of micelles and the realization of the surface-active properties of the peptide (of course, the decider does not have to know the exact values of the acidity constants of the functional groups of amino acids, but he must have an understanding of the range in which the indicator should be).

At pH 7, the total charge of the peptide is +1: deprotonation of the free carboxyl group occurs, reducing the hydrophobicity of the tail of the molecule. This leads to a decrease in the surface-active properties of the peptide, a decrease in the size of the formed micelles and an increase in the critical concentration of micelle formation compared with low pH values.

Reaching the alkaline range (pH 11) leads to deprotonation of both amino groups of lysine (pKa ~9 and 10) and the formation of a total charge of the molecule equal to -1. Now the alanine end becomes the hydrophilic head, while the branched lysine residue, deprived of charge, being the tail, sterically prevents the occurrence of optimal hydrophobic interactions. This leads to a significant increase in the critical concentration of micelle formation. The results of the reasoning can be summarized in the table for ease of perception:

pH	<i>N</i> -terminal charge (orientation)	<i>C</i> -terminal charge (orientation)			
2	+2 (head)	0			
7	+2 (head)	-1			
11	0	-1 (head)			

Due to the asymmetric structure of peptide **A**, the shape of the micelles formed on its basis differs in acidic and alkaline environments. Thus, at pH <7, peptides are collected in tubes, and at high pH values spherical aggregates are formed.

When analyzing the table from the condition, it can be noted that an increase in the concentration of the peptide gradually leads to an increase in the size of micelles (apparently within reasonable limits), but in general this knowledge is not important for solving the problem, so it is easier to limit ourselves only to the bottom line. It is also necessary to initially understand for yourself what is the dependence – direct or inverse – of the size of micelles on the surface-active properties of the peptides forming them.

An indication of the value of critical micelle formation concentrations is additional information that is not necessary for the solution; the main thing is to guess how this parameter is related to the ability of peptides to self-organize.

**5.** In the case of the Ala-Ala-Ala-Ala-Ala-Ala-Lys peptide, optimal charge separation is disrupted at different pH values. For example, at pH 7, both ends of the peptide carry charges: the N-terminal alanine has a charge of +1, whereas the lysine residue contains a deprotonated carboxyl and a protonated amino group. In this problem, it is prominently shown how sometimes it is critically important which amino acid residues are located at the *N*- and *C*-ends of a peptide.

**6.** In the presence of a hydrophobic drug in such micelles, the passage of the drug through the patient's stomach, the contents of which are characterized by low pH values, will be unhindered, followed by the destruction of micelles in the alkaline environment of the small intestine. In turn, peptide micelles formed in an alkaline environment can be used to deliver drugs to tumors (although not all) or foci of inflammation, which are usually characterized by lower pH values.

Oligopeptides have significant advantages over synthetic surfactants: they undergo biodegradation to form ordinary amino acids, and there is no immune response against them due to the small size of the molecules and the poor amino acid composition (in our case, it's all alanine residues).

#### (Russian IChO-2012 Selection Camp, Problem 3)

Note that Table 1 shows five oligopeptides that contain a total of 42 amino acid residues. Thus, the first step is to understand the reason for the absence of two residues in the first table. The only reasonable explanation is that decapeptide  $N_2$ , devoid of phenylalanine, actually contains twelve amino acid residues, the penultimate of which is the same phenylalanine. In addition, the equality of the number of phenylalanine residues in **Z** and the number of daughter oligopeptides (five each) indicates that **Z** is a cyclic homodetic polypeptide.

To stitch the peptides from the first table together in the correct order, it is necessary to use the results of  $\mathbf{Z}$  treatment with sodium in ammonia. Some of the peptides from the second table have no analytical value, since they are located inside the daughter peptides obtained by processing  $\mathbf{Z}$  with papain (highlighted in bold), but the other, reflected in the usual font, allows you to form correct crosslinking:

The peptide						Stitches peptides from Table 1			
number	1	2	3	4	5	6	7		
6	Thr	Ser	Phe	Lys	Ile	Asn	Gly	2 + 4	
7	Ser	Phe	Gln	Tyr	Asp	Arg		1 + 5	
8	His	Ala	Cys	Ile	Asp	Phe		-	
9	Cys	Lys	Val	Cys	Met	Lys		-	
10	Phe	His	Val	Met				5 + 2	
11	Arg	Trp	Phe	Glu				-	
12	Glu	Asn	Gly	Leu				-	

Then it is not difficult to determine the sequence of daughter peptides in  $\mathbb{Z}$ , it looks like 1-5-2-4-3-1, i.e., as we assumed, it is looped on itself. The amino acid lost in the first table, lysine (Lys), is found in the structure of daughter peptide No6. The complete amino acid sequence of  $\mathbb{Z}$  is as follows:

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
	Lys	Val	Cys	Met	Lys	Pro	Ser	Phe	Gln	Tyr	Asp	Arg	Pro	Phe	His	
44	Cys			1				1		1	1			1	Val	16
43	Pro														Met	17
42	Phe														Pro	18
41	Asp														Glu	19
40	Ile														Asn	20
39	Cys														Gly	21
38	Ala														Leu	22
	His	Pro	Glu	Phe	Trp	Arg	Pro	Gly	Asn	Ile	Lys	Phe	Ser	Thr	Pro	
	37	36	35	34	33	32	31	30	29	28	27	26	25	24	23	

At the same time, it should be understood that the numbering of amino acid residues in  $\mathbb{Z}$ , given above, is conditional due to its cyclicity and the impossibility of choosing a reference point. The results of treatment with *N*-bromosuccinimide confirm the earlier conclusions. First, only in the case of a cyclic structure, processing of a peptide containing two fragmentation loci (one tyrosine and tryptophan residue each) leads to two (rather than three in the case of a linear biomolecule) daughter peptides. The sequence lengths of both peptides obtained are really close – 21 and 23 amino acid residues.

(International Mendeleev Chemistry Olympiad, 2007, the 1<sup>st</sup> exam, Problem 5)

1.  ${}^{40}\text{K} \rightarrow {}^{40}\text{Ca} + e$  ( $\beta$ -decay)  ${}^{40}\text{K} + e \rightarrow {}^{40}\text{Ar}$  ( $\beta$ -capture)

2. Calcium, unlike argon, is a part of rocks, so the accuracy of determining the age of calcium will be low. When calculating, it is necessary to take into account the possibility of air entrapment in solid rock.

3. 
$$T = \frac{ln2}{k_1 + k_2} = \frac{ln2}{\frac{ln2}{T_1} + \frac{ln2}{T_2}} = \frac{T_1 T_2}{T_1 + T_2} = \frac{1.47 \cdot 10^9 \cdot 1.19 \cdot 10^{10}}{1.47 \cdot 10^9 + 1.19 \cdot 10^{10}} = 1.31 \cdot 10^9 \text{ years}$$

4. 
$$\frac{N(K \to Ca)}{N(K \to Ar)} = \frac{T_2}{T_1} = 8.1$$
  $N(K \to Ar) = \frac{1}{1+8.1} \cdot 100 = 11$ 

5. The total amount of potassium-40 in the earth's crust at the present time:

$$n({}^{40}K) = \frac{5 \cdot 10^{25} \cdot 0.015 \cdot 0.000119}{40} = 2.2 \cdot 10^{18} \text{ mol}$$

The total amount of potassium-40 at the initial moment of time, that is, 5 billion years ago:

$$n_0\binom{40}{K} = n\binom{40}{K} \cdot e^{(k_1 + k_2)t} = 2.2 \cdot 10^{18} \cdot e^{\left(\frac{\ln 2}{1.47 \cdot 10^9} + \frac{\ln 2}{1.19 \cdot 10^{10}}\right) \cdot 5 \cdot 10^9} = 3.1 \cdot 10^{19} \, mol$$

During the lifetime of the Earth,  $3.1 \cdot 10^{19} - 2.2 \cdot 10^{18} = 2.9 \cdot 10^{19}$  mol of potassium-40 decayed, of which  $2.9 \cdot 10^{19} \cdot 0.11 = 3.2 \cdot 10^{18}$  mol decayed with the formation of argon.

$$V(\mathrm{Ar}) = vV_m = 3.2 \cdot 10^{18} \cdot 22.4 \cdot 10^{-3} = 7.2 \cdot 10^{16} \mathrm{m}^3.$$

The volume of argon in the Earth's atmosphere:  $V_{\text{atm}}(\text{Ar}) = 0.01 \cdot 40 \cdot 10^9 = 4 \cdot 10^8 \text{ km}^3 = 4 \cdot 10^{17} \text{ m}^3$ . A significant proportion of argon in the atmosphere (more than 1/6) was formed during the decay of potassium-40.

6. The total amount of potassium-40 in the sample:

$$n({}^{40}K) = \frac{1000 \cdot 0.0324 \cdot 0.000119}{39} = 9.9 \cdot 10^{-5} \, mol$$

The amount of argon generated:  $n({}^{40}K) = \frac{5.9 \cdot 10^{15}}{6.0 \cdot 10^{23}} = 9.8 \cdot 10^{-9} mol$ 

The total amount of potassium decayed during time *t*:  $n_{decay} {\binom{40}{K}} = \frac{9.8 \cdot 10^{-9}}{0.11} = 8.9 \cdot 10^{-8} \text{ mol}$ Let us apply the law of radioactive decay:

$$n({}^{40}K) = \left(n_{decay}({}^{40}K) + n({}^{40}K)\right)e^{-(k_1+k_2)t} = \left(n_{decay}({}^{40}K) + n({}^{40}K)\right)e^{-t\ln 2/T}$$
$$t = \frac{T}{\ln 2} \cdot \ln\left(\frac{n_{decay}({}^{40}K) + n({}^{40}K)}{n({}^{40}K)}\right) = \frac{1.31 \cdot 10^9}{\ln 2} \cdot \ln\left(\frac{8.9 \cdot 10^{-8} + 9.9 \cdot 10^{-5}}{9.9 \cdot 10^{-5}}\right) = 1.7 \cdot 10^6 \text{ years}$$

The 2<sup>nd</sup> ARBIChO – Solutions to preparatory problems

This time is considered the age of human race.

(International Mendeleev Chemistry Olympiad, 2013, the 1<sup>st</sup> exam, Problem 5)

**1.** From the formula  $-dN / dt = \lambda N$  one can find  $\lambda = \ln 2 / T_{\frac{1}{2}}$ , thus  $T_{\frac{1}{2}} = N \cdot \ln 2 / (-dN / dt) = 1.592 \cdot 10^5$  years. From the law of radioactive decay:

$$m(t) = m(0) \cdot e^{-\lambda t} \Rightarrow m(0) - nM_{c} = m(0) \cdot 2^{-\frac{t}{T_{1}}} \Rightarrow M_{c} = \frac{m(0)}{n} \left(1 - 2^{-\frac{t}{T_{1}}}\right),$$

where m(0) – the initial mass of the sample, m(t) – current weight,  $nM_{\rm C}$  – the mass decayed during the time t,  $M_{\rm C}$  – molar mass  ${\rm C}$ . The number of moles n of the released helium equals to the number of moles of the decayed element  ${\rm C}$ .  $M_C = \frac{1-2^{-\frac{5}{1592}}}{9.333 \cdot 10^{-6}} = 233$  g/mol. Then, 233/2.533 = 92, so  ${\rm C}$  means uranium. Francium-221 is produced from uranium-233 in the course of three  $\alpha$ - and one  $\beta$ -decay, therefore X3, X4 and X5 –  $\alpha$ -decays. Then  ${\rm D}$  – is thorium-229,  ${\rm E}$  – is radium-225,  ${\rm F}$  – actinium-225.

2. On the basis of data about the content of **I** in the minerals:

$$0.6 = \frac{M_I}{M_I + M_{As} + xM_s} = \frac{M_I}{M_I + 75 + 32x}$$
$$0.286 = \frac{4M_I}{4M_I + 3M_{Hq} + xM_{Sb} + 8M_{As} + 20M_s} = \frac{4M_I}{4M_I + 1843 + 122x}$$

Solving the set of equations with two unknown quantities: x = 2;  $M_I = 209$  g/mol, 209/2.58 = 81. I – thallium, lorandite – TlAsS<sub>2</sub>, vrbaite – Tl<sub>4</sub>Hg<sub>3</sub>Sb<sub>2</sub>As<sub>8</sub>S<sub>20</sub>. The difference in mass numbers is 213 - 209 = 4 a.m.u. In this series thallium-209 is formed from bismuth-213 at  $\alpha$ -decay. X7 –  $\alpha$ -decay.  $\beta$ -decay of thallium-209 gives plumbum-209 – J.

3. The activity of the sample equals to the sum of the activities of isotopes:

$$\sum_{i} A_{i} = \sum_{i} \frac{dN_{i}}{dt} = \sum_{i} \frac{\lambda_{i} N_{i} dt}{dt} = \sum_{i} \lambda_{i} N_{i}$$

One can determine how many grams A1 and A2 decayed during the time *t*:

$$ln\frac{m\cdot\omega_{A1}}{m\cdot\omega_{A1}-x_{A1}} = \frac{ln2}{T_{\frac{1}{2}}(A1)}t \qquad ln\frac{3\cdot0.35}{3\cdot0.35-x_{A1}} = \frac{0.693}{2.1\cdot24} \cdot 12 = 0.165 \quad x_{A1} = 0.159 \ g$$
$$ln\frac{1.95}{1.95-x_{A2}} = \frac{0.693}{4.4\cdot24} \cdot 12 = 0.079 \qquad x_{A2} = 0.148 \ g$$

The 2<sup>nd</sup> ARBIChO – Solutions to preparatory problems

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$$A = \frac{x_1}{M_1} \cdot N_A \cdot \lambda_1 + \frac{x_2}{M_2} \cdot N_A \cdot \lambda_2 = \frac{N_A \ln 2}{24 \cdot 3600} \left( \frac{1.05 - x_1}{M_1} \cdot \frac{1}{T_{\frac{1}{2}}(A_1)} + \frac{1.95 - x_2}{M_2} \cdot \frac{1}{T_{\frac{1}{2}}(A_2)} \right),$$

where A – is activity,  $N_A$  – Avogadro's number.  $M_{A1} = M_A + 1$ ,  $M_{A2} = M_A - 3$ . By substituting these ratios in the expression for the activity of the sample and solving the resulting quadratic equation  $M_A = 237$  g/mol. Thus A is neptunium-237.

4. As X1 –  $\alpha$ -decay, then **B** – is protactinium-233, therefore X2 –  $\beta$ -decay. Bismuth-209 is formed by  $\beta$ -decay of plumbum-209. X10 –  $\beta$ -decay. Since **J** is obtained from the **K** in two different ways, it is obvious that in one case it is  $\alpha$ -decay, and then  $\beta$ -decay, in the second case – vice versa. X7 = X9 –  $\alpha$ decay, and X8 –  $\beta$ -decay. Plumbum-209 is formed by the decay of polonium-213 – **H**. It is formed by  $\beta$ -decay of **K** – bismuth-213. It is formed as a result of  $\alpha$ -decay of the astatine-217 – **G**. 213 – 209 = 4 a.m.u., X9 –  $\alpha$ -decay. Astatine-217 is formed by the decay of Francium-221, 221 – 217 = 4 a.m.u., X6 –  $\alpha$ -decay.

**5.** 
$$^{237}_{93}Np \rightarrow ^{233}_{91}Pa + ^{4}_{2}He \qquad ^{209}_{81}Tl \rightarrow ^{209}_{82}Pb + \beta^{-} + \tilde{v}$$

6. The mass deficiency of the nucleus (z - the nucleus charge, A - mass number):  $\Delta m = m_{\text{nuc}} - zm_{\text{p}} - (A - z)m_{\text{n}} \qquad m_{\text{nuc}} = m_{\text{A}} - zm_{\text{e}} \qquad \Delta m = -1.76122 \text{ a.m.u.}$ 1 a.m.u.(eV) = 1 a.m.u.(kg)  $\cdot c^2 / 1.602 \cdot 10^{-19} = 931.59 \text{ MeV}$  $E_{\text{b}} = \Delta m \cdot c^2, E_{\text{b.av.}} = E_{\text{b}} / \text{A} = 1.76122 \cdot 931.59 / 209 = 7.85 \text{ MeV}.$ 

(International Chemistry Olympiad, 2009, Problem 5)

1.



2. NaOH or the formula of another suitable base.





7.





also fits the data

8.



9.



10.



11.



(Uzbekistan IChO-2022 Selection Camp)

#### 1.

Α	В	С	D	Ε
<i>FeO</i> <sub>4</sub> <sup>2-</sup>	$[Fe(H_2O)_6]^{3+}$	$[Fe(H_2O)_5OH]^{2+}$	$[Fe(H_2O)_4(OH)_2]^+$	$[Fe(H_2O)_3(OH)_3]$
F	G	Н	Ι	
$[Fe(H_2O)_2(OH)_4]^-$	$[Fe(H_2 0)_6]^{2+}$	$[Fe(H_2O)_5OH]^+$	Fe	

2. 
$$E(FeO_4^{2-}/Fe) = \frac{3 \cdot 0.374 + 3 \cdot (-0.726)}{3+3} = -0.176 V.$$

$$\operatorname{FeO_4}^{2-} \xrightarrow{1.90 \text{ V}} \left[\operatorname{Fe}(\text{H}_2\text{O})_6\right]^{3+} \xrightarrow{0.77 \text{ V}} \left[\operatorname{Fe}(\text{H}_2\text{O})_6\right]^{2+} \xrightarrow{-0.44 \text{ V}} \operatorname{Fe}^{-2} \left[\operatorname{Fe}(\text{H}_2\text{O})_6\right]^{2+} \left[\operatorname{Fe}(\text{H}_2\text{O})_6\right]^{2+} \operatorname{Fe}^{-2} \left[\operatorname{Fe}(\text{H}_2\text{O})_6\right]^{2+} \left[\operatorname{Fe}(\text{H}_2\text{O}$$

- 4. The correct answer is B.
- 5. The correct answer is D.
- 6.  $FeO_4^{2-} + 3e + 8H^+ + 2H_2O = [Fe(H_2O)_6]^{3+}$ . Using the Nernst equation, we obtain:

$$E = 1.90 + \frac{0.039}{3} lg[H^+]^8 = 1.90 - 0.157 pH, a = 1.90 and b = -0.157.$$

7.  $FeO_4^{2-} + 3e + 6H_2O = [Fe(H_2O)_2(OH)_4]^- + 4OH^-$ . Using the Nernst equation, we obtain:

 $E = 0.374 + \frac{0.059}{3} lg \frac{1}{[OH^-]^4} = 0.374 + \frac{0.059 \cdot 4}{3} lg \frac{[H^+]}{K_w} = 0.374 + \frac{0.059 \cdot 4}{3} lg[H^+] - \frac{0.059 \cdot 4}{3} lgK_w = 1.475 - 0.079 pH, a = 1.475 and b = -0.079.$ 

8.  $O_2 + 4e + 4H^+ = 2H_2O \rightarrow E(O_2, 4H^+/2H_2O) = 1.23 + \frac{0.059}{4}lg[H^+]^4 = 1.23 - 0.059pH.$ 

$$2H^+ + 2e = H_2 \rightarrow E(2H^+/H_2) = 0 + \frac{0.059}{2}lg[H^+]^2 = -0.059pH.$$



**9.** At pH = 7.0,  $E(O_2, 4H^+/2H_2O) = 1.23 - 0.059 \cdot 7 = 0.817 V$ ,  $E(2H^+/H_2) = -0.059 \cdot 7 = -0.413 V$ .

From the Pourbaix diagram of iron, it can be understood that in the range of the electrode potentials  $-0.413 \div 0.817$  particles **E** ([ $Fe(H_2O)_3(OH)_3$ ]) and **G** ([ $Fe(H_2O)_6$ ]<sup>2+</sup>) will be stable.

(International Mendeleev Chemistry Olympiad, 2013, the 2<sup>nd</sup> exam, Physical Chemistry, Problem 3)

- 1.  $HSO_{\overline{4}} + 3H^+ + 2e^- = H_2SO_3 + H_2O;$   $HSO_{\overline{4}} + 5H^+ + 4e^- = 0.5H_2S_2O_3 + 2.5H_2O;$  $HSO_{\overline{4}} + 7H^+ + 6e^- = S + 4H_2O;$   $HSO_{\overline{4}} + 9H^+ + 8e^- = H_2S + 4H_2O.$
- 2.  $E_{\text{HSO}_{7}}^{0} = E_1, \ E_{\text{S/H}_2\text{S}}^{0} = E_2. \ F = 96500 \ \text{Cl} \cdot \text{mol}^{-1} \text{Faraday constant.}$

Half-reaction	$\Delta G^0$
$HSO\overline{4} + 7H^+ + 6e^- = S + 4H_2O$	$\Delta G_1^0 = -6FE_1$
$S + 2H^+ + 2e^- = H_2S$	$\Delta G_2^0 = -2FE_2$

 $HSO_{\overline{4}} + 9H^{+} + 8e^{-} = H_2S + 4H_2O$   $\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0 = -8FE_3$ 

The third half-reaction is the sum of the first and the second ones, thus the Gibbs energy can be evaluated by addition  $\Delta G_1$  and  $\Delta G_2$ .  $E_3 = \frac{6 \cdot 0.386 + 2 \cdot 0.144}{8} = 0.326$  V.

**3.** Among four redox potentials only  $E_{HSO_4/S}^0 > E_{Cu^{2+}/Cu}^0$ . Thus, copper dissolves and the acid reduces to S.

**4.** To evaluate Gibbs energy, the same method can be used. The disproportionation reaction can be considered as a difference of half-reactions given in the diagram.

	Half-reaction	$\Delta G^0$
	$H_2SO_3 + 2H^+ + 2e^- = 0.5H_2S_2O_3 + 1.5H_2O$	$\Delta G_1^0 = -2FE_1 \ (E_1 = E_{H_2SO_3/\frac{1}{2}H_2S_2O_3}^0)$
	$0.5H_2S_2O_3 + 2H^+ + 2e^- = S + 1.5H_2O$	$\Delta G_2^0 = -2FE_2 \ (E_2 = E_{\frac{1}{2}H_2S_2O_3/S}^0)$
	$H_2S_2O_3 = S + H_2SO_3$	$\Delta G_3^0 = \Delta G_2^0 - \Delta G_1^0$
Δ	$G_3^0 = 2F \cdot (E_1 - E_2) = 2 \cdot 96500 \cdot (0.4 - 0.6) = -$	-38600 J·mol <sup>-1</sup> .

5. At pH 14, half-reaction for reduction is:  $0.5S_2O_3^2 + 1.5H_2O + 2e^- = S + 3OH^-$ .

Half-reaction	$\Delta G^0$
$0.5H_2S_2O_3 + 2H^+ + 2e^- = S + 1.5H_2O$	$\Delta G_1^0 = -2F E_{\frac{1}{2}H_2S_2O_3/S}^0 = -115.8 \text{ kJ} \cdot \text{mol}^{-1}$
$H_2S_2O_3 = 2H^+ + S_2O_3^2 -$	$\Delta G_2^0 = - RT \cdot \ln(K_{a1}K_{a2}) = 13.23 \text{ kJ} \cdot \text{mol}^{-1}$
$H_2O = H^+ + OH^-$	$\Delta G_3^0 = -RT \cdot ln(K_w) = 79.87 \text{ kJ} \cdot mol^{-1}$
$0.5S_2O_3^2 + 1.5H_2O + 2e^- = S + 3OH^-$	$\Delta G_4^0 = \Delta G_1^0 - 0.5 \Delta G_2^0 + 3 \Delta G_3^0 = 117.2 \text{ kJ} \cdot \text{mol}^{-1}$

At pH 14 the acid (pK<sub>a1</sub> = 0.60, pK<sub>a2</sub> = 1.7) completely dissociates. The last chemical equation is the linear combination of the three other in acidic medium: acid reduction and dissociation and water dissociation  $E_{\frac{1}{2}s_{2}O_{2}^{2}/5}^{0} = \frac{117200}{2 \cdot 96500} = -0.607 \text{ V}.$ 

To evaluate Gibbs energy for disproportionation the same method as in **4** can be used  $\Delta G^{0} = 2F(E_{1} - E_{2}) = 2 \cdot 96500 \cdot (-0.397 + 0.414) = +3281 \text{ J} \cdot \text{mol}^{-1}.$  The equilibrium constant is  $K = \exp(-\frac{\Delta G^{0}}{RT}) = 0.266. \text{ S}_{2}\text{O}_{3}^{2-} = \text{S} + \text{SO}_{3}^{2-}, \text{K} = \frac{[\text{SO}_{3}^{2-}]}{[\text{S}_{2}\text{O}_{3}^{2-}]},$ 

$$[S_2O_3^{2-}] + [SO_3^{2-}] = c_0 = 1 \cdot 10^{-3} \text{ M Then } [S_2O_3^{2-}] = \frac{c_0}{1+K} = \frac{1 \cdot 10^{-3}}{1+0.266} = 7.90 \cdot 10^{-4} \text{ M.}$$

## The 2<sup>nd</sup> ARBIChO – Solutions to preparatory problems

(International Chemistry Olympiad, 1997, Problem 5)

- **1.** Calculation of the atomic radius of iron (expressed in cm).
- **2.** Calculation of its density (expressed in  $g \text{ cm}^{-3}$ ) at 1250 K.

Expected steps of the calculation:

- 1. Define the length a, b, c,  $d_1$ ,  $d_2$ , and r and volume  $V_1$  and  $V_2$  parameters for both bcc and fcc structures of iron (*cf.* Details below).
- 2. Calculate the volume  $V_1$  of the unit cell of  $\alpha$ -iron from its density  $\rho_{bcc}$  at 293 K, the molar weight M(Fe) of iron, and Avogadro's number  $N_A$ .
- 3. Calculate the length  $d_1$  of the edge of the bcc unit cell from its volume  $V_1$ .
- 4. Calculate the atomic radius r of iron from the length "d<sub>1</sub>".
- Calculate the length d<sub>2</sub> of the edge of the fcc unit cell at 1250 K from the atomic radius r of iron.
- 6. Calculate the volume  $V_2$  of the fcc unit cell of  $\gamma$ -iron from the length  $d_2$  of its edge.
- 7. Calculate the mass *m* of the number of iron atoms in a unit cell of  $\gamma$ -iron from the molar weight *M*(Fe) of iron and Avogadro's number *N*<sub>A</sub>.
- 8. Calculate the density  $\rho_{fcc}$  of  $\gamma$ -iron from the values of "*m*" and " $V_2$ ".

An alternative route to  $\rho_{fcc}$  of  $\gamma$ -iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

- 5'. Calculate the percent space filling ratio of the bcc unit cell.
- 6'. Calculate the percent space filling ratio of the fcc unit cell.
- 7'. Calculate the  $\rho_{fcc}/\rho_{bcc}$  density ratio from the fcc/bcc space filling ratios.
- 8'. Calculate the density  $\rho_{fcc}$  of  $\gamma$ -iron from the value found in step 7'.



Body centered cubic structure (bcc)



Face-centered cubic structure (fcc)

#### Calculations in details

At 293 K,  $\alpha$ -iron has a bcc crystal structure.

Each unit cell possesses 2 atoms and one of them is in the center of the cell.

At 1250 K,  $\gamma$ -iron has a fcc crystal structure.

Each unit cell possesses 4 atoms and each side has one-half an atom at its center. r =

atomic radius of iron. a = length of the diagonal on one side of the bcc unit cell.

b = length of the diagonal passing through the center of the bcc unit cell. c =

length of the diagonal on one side of the fcc unit cell.  $d_1 =$  length of the edge of the bcc unit cell of  $\alpha$ -iron.

 $d_2$  = length of the edge of the fcc unit cell of  $\gamma$ -iron.

 $V_1$  = Volume of the bcc unit cell of  $\alpha$ -iron.

 $V_2$  = Volume of the fcc unit cell of  $\gamma$ -iron.

 $V_{\rm a}$  = Volume of one atom.

 $V_{a1}$  = Volume occupied by 2 atoms in one bcc unit cell.

 $V_{a2}$  = Volume occupied by 4 atoms in one fcc unit cell.

 $R_1$  = Percent space filling ratio in a bcc unit cell.

 $R_2$  = Percent space filling ratio in a fcc unit cell.

$$V_{a} = (4/3) \pi r^{3} \qquad V_{a1} = 2 V_{a} \qquad V_{a2} = 4 V_{a} \qquad b = 4 r;$$
  

$$a^{2} = 2 d_{1}^{2}; \qquad b^{2} = d_{1}^{2} + a^{2} = 3 d_{1}^{2} \qquad d_{1} = (b^{2}/3)^{1/2} = (16 r^{2}/3)^{\frac{1}{2}};$$
  

$$V_{1} = d_{1}^{3} = [(16 r^{2}/3)^{\frac{1}{2}}]^{3} \qquad c = 4 r; \qquad c^{2} = 2 d_{2}^{2}$$
  

$$d_{2} = (c^{2}/2)^{\frac{1}{2}} = (16 r^{2}/2)^{\frac{1}{2}}; \qquad V_{2} = d_{2}^{3} = [(16 r^{2}/2)^{\frac{1}{2}}]^{3}$$

2.  $1.000 \text{ cm}^3$  of iron weights 7.874 g at 293 K ( $\rho_{bcc}$ ).

1 mole of iron weights 55.847 g ( $M_{Fe}$ ).

Thus, 0.1410 mol (7.874 g / 55.847 g mol<sup>-1</sup>) of iron occupy a volume of 1.000 cm<sup>3</sup> or 1 mole of iron will occupy a volume of 7.093 cm<sup>3</sup>

1 mole corresponds to  $6.02214 \times 10^{23}$  atoms

 $V_1 = (7.093 \text{ cm}^3 \text{ mol}^{-1}) \times (2 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$  $V_1 = 2.356 \times 10^{-23} \text{ cm}^3 \text{ per unit cell}$ 

3. 
$$d_1 = (V_1)^{1/3} = (2.356 \times 10^{-23} \text{ cm}^3)^{1/3} d_1 = 2.867 \times 10^{-8} \text{ cm}^3$$

- 4. For a bcc structure, the value of  $d_1$  can be expressed as:  $d_1 = [(16 r^2)/3]^{1/2}$  so the value of "r" will be:  $r = (3 d_1^2/16)^{1/2} r = [3 (2.867 \times 10^{-8} \text{ cm})^2/16]^{1/2} r = 1.241 \times 10^{-8} \text{ cm}$
- 5. At 1250 K, in the fcc structure, the value of " $d_2$ " is given by:  $d_2 = (16 r^2/2)^{1/2}$  $d_2 = [16 (1.241 \times 10^{-8} \text{ cm})^2/2]^{1/2} d_2 = 3.511 \times 10^{-8} \text{ cm}$
- 6.  $V_2 = d_2^3 = (3.511 \times 10^{-8} \text{ cm})^3$

 $V_2 = 4.327 \times 10^{-23} \text{ cm}^3$ 

7. The mass "*m*" of the 4 iron atoms in the fcc unit cell will be:

 $m = (55.847 \text{ g mol}^{-1}) \times (4 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$ 

 $m = 3.709 \times 10^{-22}$  g per unit cell

8.  $\rho_{fcc} = m / V_2 = (3.709 \times 10^{-22} \text{ g}) / (4.327 \times 10^{-23} \text{ cm}^3) \rho_{fcc} = 8.572 \text{ g/cm}^3$ Alternative route to  $\rho_{fcc}$  of  $\gamma$ -iron:

5'. 
$$\mathbf{R}_1 = [(V_{a1}) / (V_1)] \times 100\% = [(2 V_a) / (V_1)] \times 100\%$$

## The 2<sup>nd</sup> ARBIChO – Solutions to preparatory problems

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$$R_{1} = ([2 \times (4/3) \pi r^{3}] / [(16 r^{2}/3)^{1/2}]^{3}) \times 100\%$$

$$R_{1} = ([(8/3) \pi r^{3}] / [(16/3)^{3/2} r^{3}]) \times 100\%$$

$$R_{1} = ([(8/3) \pi] / [(16/3)^{3/2}]) \times 100\%$$

$$R_{1} = [(8.378) / (12.32)] \times 100\%$$

$$R_{1} = 68.02 \%$$

6'. 
$$R_{2} = [(V_{a2}) / (V_{2})] \times 100\% = [(4 V_{a}) / (V_{2})] \times 100\%$$
$$R_{2} = ([4 \times (4/3) \pi r^{3}] / [(16 r^{2}/2)^{1/2}]^{3}) \times 100\%$$
$$R_{2} = ([(16/3) \pi r^{3}] / [8^{3/2} r^{3}]) \times 100\%$$
$$R_{2} = ([(16/3) \pi] / [8^{3/2}]) \times 100\%$$
$$R_{2} = [(16.76) / (22.63)] \times 100\%$$

 $R_2 = 74.05\%$ 

7'. 
$$\rho_{fcc} / \rho_{bcc} = (74.05\%) / (68.02\%)$$
  
 $\rho_{fcc} / \rho_{bcc} = 1.089$ 

8'. 
$$\rho_{fcc} = 1.089 \times \rho_{bcc}$$
  
 $\rho_{fcc} = 1.089 \times 7.874 \text{ g cm}^{-3}$   
 $\rho_{fcc} = 8.572 \text{ g cm}^{-3}$ 

**3.** Calculation of the average number of carbon atoms per unit cell of  $\alpha$ -iron in martensite containing 4.3 % C by mass.

**4.** Calculation of the density (expressed in  $g \text{ cm}^{-3}$ ) of this material.

Expected Steps of the Calculation:

- 1. From the percent composition of martensite (by mass), calculate the relative amounts of moles of carbon and iron.
- 2. Bring the C/Fe molar ratio to one (1) unit cell (Note: 2 Fe atoms per unit cell).
- 3. Find the smallest whole number of C atoms for the smallest whole number of unit cell (facultative).

# The 2<sup>nd</sup> ARBIChO – Solutions to preparatory problems

- 4. Calculate the mass of iron per unit cell.
- 5. Calculate the mass of carbon per unit cell.
- 6. Calculate the total mass of carbon and iron in one unit cell.
- Calculate the density of martensite [ρ(martensite at 4.3 %C)] from the total mass of C and Fe and volume (V<sub>1</sub>) of α-iron bcc unit cell.

Details:

1. In 100.0 g of martensite at 4.3 % C:  $(4.3 \text{ g C}) / (12.011 \text{ g mol}^{-1}) = 0.36 \text{ mol C}$ 

 $(95.7 \text{ g Fe}) / (55.847 \text{ g mol}^{-1}) = 1.71 \text{ mol Fe}$ 

So we have 1 carbon atom for 4.8 iron atoms or

0.21 carbon atoms per iron atom.

2. Martensite has a "bcc" crystal structure (2 iron atoms per unit cell).

 $[(1 \text{ C atom}) / (4.8 \text{ Fe atoms})] \times (2 \text{ Fe atoms} / \text{unit cell}) \text{ or:}$ 

0.42 carbon atoms per unit cell

5 carbon atoms [ $(0.42 \text{ C} \text{ atom } / 0.42) \times 5$ ] in 12 unit cells [ $(1 \text{ unit cell}/0.42) \times 5$ ].

5 carbon atoms dispersed in 12 unit cells

- 3.  $[(55.847 \text{ g/mol}) / (6.02214 \times 10^{23} \text{ atoms/mol})] \times (2 \text{ atoms/unit cell of } \alpha\text{-iron})$ 1.8547×10<sup>-22</sup> g Fe per unit cell of  $\alpha$ -iron
- 4.  $(12.011 \text{ g/mol}) / (6.02214 \times 10^{23} \text{ atoms/mol})$

 $1.9945 \times 10^{-23}$  g C per atom

5.  $[1.8547 \times 10^{-22} \text{ g Fe} + (0.42 \text{ C at.} \times 1.9945 \times 10^{-23} \text{ g / C at.})]$  per unit cell

 $1.938 \times 10^{-22}$  g C and Fe per unit cell

Each unit cell of  $\alpha$ -iron occupies a volume,  $V_1 = 2.356 \times 10^{-23}$  cm<sup>3</sup> (*cf.* Question i)

 $\rho$ (martensite at 4.3 % C) = (1.938×10<sup>-22</sup> g C and Fe) / (2.356×10<sup>-23</sup> cm<sup>3</sup>)

 $\rho$ (martensite at 4.3 % C) = 8.228 g cm<sup>-3</sup>

(International Chemistry Olympiad, 2000, Problem 2)

1.  $\Delta H^0 = -1575.0 \text{ kJ mol}^{-1} + 1.5 \times (-241.8) \text{ kJ mol}^{-1} - (-2021.0 \text{ kJ mol}^{-1}) = 83.3 \text{ kJ mol}^{-1}$   $n = m / M = 1000 \text{g} / 172.18 \text{ g mol}^{-1} = 5.808 \text{ mol}$  $\Delta H^0 = 484 \text{ kJ}$ 

The reaction is endothermic.

2. 
$$\Delta S^{0} = 130.5 \text{ J K}^{-1} \text{ mol}^{-1} + 3/2 \times 188.6 \text{ J K}^{-1} \text{ mol}^{-1} - 194.0 \text{ J K}^{-1} \text{ mol}^{-1}$$
  
 $= 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $\Delta G^{0} = \Delta H^{0} - T\Delta S^{0} = 17886 \text{ J mol}^{-1}$   
 $\Delta G^{0} = -RT \ln K$   
 $K = (p(\text{H}_{2}\text{O}))^{3/2} = 7.35 \times 10^{-4} \text{ (pressure in bar)}$   
 $p(\text{H}_{2}\text{O}) = 8.15 \times 10^{-3} \text{ bar}$ 

**3.**  $p(H_2O) = 1.00$  bar implies K = 1.00 and  $\Delta G^0 = -RT \ln K = 0$ 

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

$$0 = 83300 \text{ J K}^{-1} - T 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 380 \text{ K or } 107 \text{ }^{\circ}\text{C}$$

- 4.  $E^{0}(\text{cell}) = E^{0}(\text{right}) E^{0}(\text{left}) = 0.40 \text{ V} (-0.44 \text{ V}) = 0.84 \text{ V}$
- 5. Oxidation takes place at the negative, left half-cell. Left half:  $2 \text{ Fe} \rightarrow 2 \text{ Fe}^{2+} + 4 \text{ e}^{-1}$ (multiplied by 2)

Right half:  $O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$ 

Overall:  $2 \operatorname{Fe} + \operatorname{O}_2 + 2 \operatorname{H}_2\operatorname{O} \rightarrow 2 \operatorname{Fe}^{2+} + 4 \operatorname{OH}^{-}$ 

6.  $K = [Fe^{2+}]^2 [OH^{-}]^4 / p(O_2)$  (conc. in M and pressure in bar)

 $\Delta G = -n F E \text{ (cell)} = -RT \ln K$ 

$$K = 6.2 \times 10^{56}$$

7.  $Q = It = 0.12 \text{ A} \times 24 \times 60 \times 60 \text{ s} = 10368 \text{ C}$ 

$$n(e^{-}) = Q / F = 10368 \text{ C} / 96485 \text{ C} \text{ mol}^{-1} = 0.1075 \text{ mol}$$

$$m(\text{Fe}) = n(\text{Fe}) \times M(\text{Fe}) = 1/2 \times 0.1075 \text{ mol} \times 55.85 \text{ g mol}^{-1} = 3.0 \text{ g}$$

8. 
$$E(\text{cell}) = E^{0} (\text{cell}) - \frac{0.05916 \text{ V}}{n} \log \frac{[\text{Fe}^{2+}]^{2} [\text{OH}^{-}]^{4}}{p(\text{O}_{2})}$$
  
 $pH = 9.00 \text{ implies } [\text{H}^{+}] = 1 \times 10^{-9} \text{ and } [\text{OH}^{-}] = 1 \times 10^{-5}$   
 $E(\text{cell}) = 0.84 \text{ V} - \frac{0.05916 \text{ V}}{4} \log \frac{0.015^{2} [1 \times 10^{-5}]^{4}}{0.700} = 1.19 \text{ V}$ 

(International Chemistry Olympiad, 2021, Preparatory problem 4)

1.

$$C(graphite) + O_2 \rightarrow CO_2$$
 $\Delta_c H \circ (graphite) = -393.5 \text{ kJ mol}^{-1}$  $C(diamond) + O_2 \rightarrow CO_2$  $\Delta_c H \circ (diamond) = -395.3 \text{ kJ mol}^{-1}$ Therefore, $\Delta c H \circ (diamond) = -395.3 \text{ kJ mol}^{-1}$  $C(graphite) \rightarrow C(diamond)$  $\Delta H = +1 \cdot 8 \text{ kJ mol}^{-1}$ For the reaction above, the change in entropy is  $\Delta S = -3.25 \text{ J K}^{-1} \text{ mol}^{-1}$ .

 $\Delta G = \Delta H - T \Delta S = +2.77 \text{ kJ mol}^{-1}$ 

$$\frac{1}{60}C_{60}+O_2 \rightarrow CO_2 \qquad \Delta c H^{\circ}(C_{60}) = -2596560/60 = -432.8 \text{ kJ mol}^{-1}$$
  
Therefore

I herefore,

$$C(\text{graphite}) \rightarrow \frac{1}{60} C_{60} \qquad \Delta H = +39.3 \text{ kJ mol}^{-1}$$

For the reaction above, the change in entropy is  $\Delta S = +1.54 \text{ J K}^{-1} \text{ mol}^{-1}$ .  $\Delta G = \Delta H - T \Delta S = +38.8 \text{ kJ mol}^{-1}$ 

The order of stability is thus graphite > diamond > C<sub>60</sub>.

- 2. The reaction rate is very slow due to the high activation energy.
- 3.

Cathode:	$2 \operatorname{C}(\operatorname{diamond}) + \operatorname{CaF}_2 + 2 \operatorname{e}^- \rightarrow \operatorname{CaC}_2 + 2 \operatorname{F}^-$
Anode:	$2 F^- + CaC_2 \rightarrow 2 C(graphite) + CaF_2 + 2 e^-$

4. The change in Gibbs free energy of the conversion reaction from diamond to graphite is  $\Delta G = -n F E = -1100 - 4.64T$  (*n* is the number of moles of electrons transferred per 1 mole of carbon, which is n = 1 in this case). The thermodynamic quantities for the conversion reaction one graphite to diamond are obtained by changing the sign. By comparing the result with  $\Delta G = \Delta H - T \Delta S$ , the enthalpy and entropy are found to be  $\Delta H = +1.10 \text{ kJ mol}^{-1} \text{ and } \Delta S = -4.64 \text{ J K}^{-1} \text{ mol}^{-1}.$ 



6. Left: 3R, center: 2H, right: 1H.

7. Left: lonsdaleite, right: diamond.

8. The area of the hexagonal cell that constitutes graphene is

 $1.42 \times (1.42 \times sin60^{\circ}) \times \frac{1}{2} \times 6 = 5.24 \text{ Å}^2.$ 

The number of carbon atoms within this hexagonal cell is two. Based on these values, the volume occupied by two carbon atoms (see the right figure) can be calculated as  $5.24 \times 3.35 = 17.55$  Å<sup>3</sup>.

Therefore, the density of graphite is  $\frac{12.01 \times \frac{2}{6.02 \times 10^{23}}}{17.55 \times 10^{-24}} = 2.27 \ g \ cm^{-3}$ The side length of the unit cell of a diamond is  $4/\sqrt{3}$  times the distance between covalently bonded carbon atoms, which can be calculated to be 3.56 Å.



There are eight carbon atoms in the unit cell.

Based on these values, the volume occupied by eight carbon atoms can be calculated as  $3.56^3 = 44.98 \text{ Å}^3$ .

Therefore, the density of diamond is  $\frac{12.01 \times \frac{8}{6.02 \times 10^{23}}}{44.98 \times 10^{-24}} = 3.55 \text{ g cm}^{-3}.$ 

**9.** If there is no volume change between graphite and diamond, the density of graphite and diamond should be the same. Using the results of question 8, the distance between layers can be calculated as  $3.35 \times \frac{2.27}{3.35} = 2.14$  Å

The distance between graphene layers is estimated to be as large as 2.78 Å even under 30 GPa (300,000 bar). Therefore, the direct conversion method requires high temperature in addition to high pressure to accelerate the reaction.

#### Problem 15. Mechanism of Catalysis by Lactate Dehydrogenase

(International Chemistry Olympiad, 2012, Preparatory problem 20)

rate is greatest at high pH, as in curve B.

- 1 Curve A is the reaction with pyruvate, and curve B is the reaction with lactate. Since the reaction with pyruvate involves acid as a reagent, at lower *pH* values one might expect faster reaction rates. According to Scheme 1, His-195 acts as an acid, by donating a proton to pyruvate. Thus, for the reaction with pyruvate, His-195 must be protonated at the start of the reaction. His-195 will be protonated at low *pH*, and the rate of the reaction will be highest at low *pH*, as in curve A. For the reverse reaction, His-195 acts as a base to remove a proton from lactate. In this case, His-195 must be deprotonated at the start of the reaction. The reaction.
- 2 Hydrogen bonds. The carbonyl group is polarized, with a partial negative charge on the oxygen. The partial negative charge is attracted electrostatically to the positively charged His-195 and Arg-109.
- 3 Ile-250 can be involved in dispersion interactions with the dihydronicotinamide ring. The instantaneous dipole in Ile-250 that arises due to spontaneous fluctuations of electron density induces a dipole in the dihydronicotinamide, and the two dipoles interact.
- 4 The Arg-109 end group increases the polarization of the carbonyl group of pyruvate, making it more susceptible to reaction with hydride. This accounts for the great decrease in reaction rate when Arg-109 is mutated to glutamine. This polarization is irrelevant for the sulfite reaction, so that reaction is unaffected by the mutation. Arg-109 is unlikely to be the acid that protonates pyruvate, since it is a very weak acid (pK<sub>a</sub> ~ 12.5). His-195 is more acidic (see above).

Arg-109 also seems to assist in binding pyruvate in the active site, as indicated in the figure and reflected in the 15-fold reduction in binding affinity for pyruvate.

5 The conclusion from this set of experiments is that hydrogen bonding between Asp-168 and His-195 must polarize His-195 and make it a stronger base than it would be otherwise. This is reflected in the fact that the  $pK_a$  of His-195 = 7 (see above), is somewhat greater than expected for a His residue ( $pK_a$  for His is ~6.0).

Asn should be able to form a hydrogen bond to His-195 similar to that of Asp, but that would be a weaker bond since Asn side chain is neutral whereas it is negatively charged in Asp. On the other hand, Ala is unable to form such a hydrogen bond. If the only function of Asp-168 were to hold His-195 in the proper orientation for reaction, then one would predict that the Asn mutant would be significantly more active than the Ala mutant, which is not observed.

(International Chemistry Olympiad, 2015, Preparatory problem 1)

As can be seen from the figure, there are many possible ways to go from point A (1 bar, 298 K) to point B (8 bar, 298 K) using only adiabatic and isobaric segments. The work W is equal to the area under the path. It is clear that W is minimal if we complete the process in two stages: isobaric cooling and then adiabatic compression.



We will derive a general formula to calculate the work of transformation from  $(p_1, T_1)$  to

 $(p_2, T_2)$  in two stages. If for the reversible adiabatic process  $pV^{\frac{5}{3}} = p\left(\frac{RT}{p}\right)^{\frac{5}{3}} = const$ , then  $\frac{T^{\frac{5}{3}}}{p^{\frac{2}{3}}}$ 

or  $\frac{T}{p_5^2} = const$ . After the isobaric stage, the pressure  $p_1$  and the temperature  $T = T_2 \left(\frac{p_1}{p_2}\right)^{\frac{2}{5}}$ .

The work at the adiabatic stage is  $W_2 = \Delta U = \frac{3}{2}RT_2\left(1 - \left(\frac{p_1}{p_2}\right)^{2/5}\right)$ , and at the first stage

$$W_{1} = p_{1}(V_{1} - V) = R\left(T_{1} - T_{2}\left(\frac{p_{1}}{p_{2}}\right)^{2/5}\right). \text{ In total, } W = W_{1} + W_{2} = RT_{1} + \frac{3}{2}RT_{2} - \frac{5}{2}RT_{2}\left(\frac{p_{1}}{p_{2}}\right)^{2/5}$$
  
If  $T_{1} = T_{2}$ , then  $W = \frac{5}{2}RT_{2}\left(1 - \left(\frac{p_{1}}{p_{2}}\right)^{2/5}\right).$  Thus,  $W = \frac{5}{2} \cdot 8.314 \cdot 298 \cdot \left(1 - \left(\frac{1}{8}\right)^{2/5}\right) = 3500 \text{ J.}$ 

In a reversible isothermal compression,  $W = RT \ln \left(\frac{p_2}{p_1}\right) = 5150 \text{ J}$ 

2. The maximum work is done when the first stage is adiabatic and the second one is isobaric. We can use the same formula for the reverse process and obtain the work with the opposite sign.

## The 2<sup>nd</sup> ARBIChO – Solutions to preparatory problems

$$W = -\frac{5}{2}RT_2\left(1 - \left(\frac{p_2}{p_1}\right)^{2/5}\right) = -\frac{5}{2} \cdot 8.314 \cdot 298 \cdot \left(1 - \left(\frac{8}{1}\right)^{2/5}\right) = 8040 \text{ J}$$

- 3. According to the first law of thermodynamics,  $Q = W + \Delta U = W$ . The total work done on the gas during these steps is:  $W = 3 \cdot \frac{5}{2} RT_2 \left(1 \left(\frac{1}{2}\right)^{2/5}\right) = 4500 \text{ J}.$
- 4. The maximum efficiency is achieved when the area of the cycle is the largest, i.e. when we complete the cycle in four steps: cooling, compression, heating, expansion. Then  $\eta = \frac{8040-3500}{8040} = 0.565$  All the efficiencies from 0 to 0.565 are possible, if we go in more steps.
- 5. The work *W* done on gas during cooling and compression stages can be found from equation

$$\eta = \frac{8040 - W}{8040} = 0.379; \quad W = 4993 \,\mathrm{J} \,.$$

If the number of steps is *n*, then  $x = 8^{\frac{1}{n}}$ . Since the work at each step is the same, the total work is:

 $W = n \cdot \frac{5}{2} RT_2 \left( 1 - \left(\frac{1}{8}\right)^{2/5n} \right)$ . After some calculations with different integer *n*, we find that n = 13.

$$6. \quad \eta = \frac{8040 - 3500}{8040 + 3500} = 0.393$$

(International Chemistry Olympiad, 2020, Preparatory problem 20)

- **1.**  $2\Delta r H^{\circ} = \Delta H1 + \Delta H2 + (-\Delta H3) + (-2\Delta H4) = 149.70 \text{ kJ mol}^{-1}$ .  $\Delta r H^{\circ} = 74.85 \text{ kJ mol}^{-1}$
- $2. \quad \Delta \mathbf{r} \mathbf{G}^{\circ} = \Delta \mathbf{r} \mathbf{H}^{\circ} \mathbf{T} \Delta \mathbf{r} \mathbf{S}^{\circ}$
- $= 74850 \text{ J/mol} (298\text{K}) \times (80 \text{ J mol}^{-1} \text{ K}^{-1}) \Delta r G^{\circ} =$
- $5.10 \times 10^4$  J mol<sup>-1</sup>
- **3.**  $\Delta \mathbf{r} \mathbf{G}^\circ = -\mathbf{R} \mathbf{T} \ln \mathbf{K}$
- $K = e^{-\Delta r G/RT}$
- $K = 1.14 \times 10^{-9}$
- **4.**  $ln \frac{K_f}{K_i} = -\frac{\Delta_r H}{R} \left( \frac{1}{T_f} \frac{1}{T_i} \right)$

K at 50 °C =  $1.20 \times 10^{-8}$ 

5.  $XY_4(g) \rightleftharpoons X(s) + 2Y_2(g)$ 

	XY4 (g)	X (s)	Y2 (g)
Initial amount	n	—	_
Amount of change	$-\alpha n$		2an
Final amount	$\mathbf{n} - \alpha \mathbf{n} = \mathbf{n} \ (1 - \alpha)$		2an
Mole Fraction	$\frac{1-\alpha}{1+\alpha}$		$\frac{2\alpha}{1+\alpha}$
Partial Pressures	$\frac{1-\alpha}{1+\alpha} P_{Total}$		$\frac{2\alpha}{1+\alpha} P_{Total}$

$$K = \frac{\left(\frac{P(Y_2)}{p^\circ}\right)^2}{\left(\frac{P(XY_4)}{p^\circ}\right)} = \frac{4\alpha^2}{1-\alpha^2} \times \frac{P}{p^\circ}$$

$$1-\alpha^2=1\;(\alpha<\!\!<\!\!1\;)$$

 $1.14 \times 10^{-9} = 4\alpha^2 \times 0.1$ 

- $\alpha = 5.35 \times 10^{-5}$ , percent degree of dissociation (%) = 5.35 × 10<sup>-3</sup>%
- **6.** As the temperature increases, the degree of dissociation increases. As the pressure increases, the degree of dissociation decreases.
- 7. Supercooled water at  $-20 \degree C$  (1) à Water at  $0 \degree C$  (2) à Ice at  $0 \degree C$  (3) à Ice at  $-20 \degree C$

$$\Delta S_{1} = \int_{T_{i}}^{T_{f}} \frac{dq_{\text{reversible}}}{T} = \int_{T_{i}}^{T_{f}} \frac{c_{p,m}dT}{T} = \int_{253.15}^{273.15} \frac{75.3 \text{ dT}}{T} = 75.3 \ln\left(\frac{273.15}{253.15}\right) = 5.73 \text{ J mol}^{-1} \text{ K}^{-1}$$
  

$$\Delta S_{2} = -\frac{q_{\text{freezing}}}{T} = -\frac{6020}{273.15} = -22.04 \text{ J mol}^{-1} \text{ K}^{-1}$$
  

$$\Delta S_{3} = \int_{T_{i}}^{T_{f}} \frac{dq_{\text{reversible}}}{T} = \int_{T_{i}}^{T_{f}} \frac{c_{p,m}dT}{T} = \int_{273.15}^{253.15} \frac{37.7 \text{ dT}}{T} = 37.7 \ln\left(\frac{253.15}{273.15}\right) = -2.87 \text{ J mol}^{-1} \text{ K}^{-1}$$
  

$$\Delta S_{3} = \Delta S_{1} + \Delta S_{2} + \Delta S_{3} = -19.18 \text{ J mol}^{-1} \text{ K}^{-1}$$

- **8.** The total change in entropy in the surroundings should be found by total heat given off to the surroundings
- $q=-(20K \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1})+6020 \text{ J mol}^{-1}+(20 \text{ K} \times 37.7 \text{ J mol}^{-1} \text{ K}^{-1})=5268 \text{ J mol}^{-1}$  $\Delta_{sur}S = \frac{q_{sur}}{T} = \frac{5268}{253.15} = 20.81 \text{ J mol}^{-1} \text{ K}^{-1}$
- 9.  $\Delta$ universeS =  $\Delta$ sysS +  $\Delta$ surS = 1.63 J mol<sup>-1</sup> K<sup>-1</sup>

(International Chemistry Olympiad, 2009, Problem 6)

1

	Number	of predicted geometrica	l isomers
	Hexagonal planar X	Trigonal Prismatic Y	Octahedral Z
MA <sub>6</sub>	1	1	1
MA <sub>5</sub> B	1	1	1
MA <sub>4</sub> B <sub>2</sub>	3	3*	2
MA <sub>3</sub> B <sub>3</sub>	3	3*	2
MA <sub>4</sub> (C-C)	1	2	1
MA <sub>2</sub> (C-C) <sub>2</sub>	2	4*	2*
M(C-C) <sub>3</sub>	1	2	1*







6  $n(Ag^{+}) = 0.100 \text{ mol } dm^{-3} \times 0.0228 \text{ dm}^{3} = 2.28 \cdot 10^{-3} \text{ mol}$   $n(CI^{-}) = 2.28 \cdot 10^{-3} \text{ mol}$   $m(CI) = 8.083 \cdot 10^{-2} \text{ g}$ %  $CI = \frac{8.083 \cdot 10^{-2} \text{ g}}{0.2872 \text{ g}} \times 100 = 28.1$ 

7 n(KOH) = 0.0124 mol

5

n(HCI) neutralised by ammonia = 0.025 mol – 0.0124 mol = 0.0126 mol m(NH<sub>3</sub>) = 17.034 g mol<sup>-1</sup> × 0.0126 mol = 0.2146 g

% NH<sub>3</sub> =  $\frac{0.2146 \text{ g}}{0.7934 \text{ g}} \times 100 = 27.1 \%$ 

- $\textbf{8} \quad \text{Co}_2\text{O}_3 + 2 \text{ KI} + 6 \text{ HCI } \rightarrow 2 \text{ CoCl}_2 + \text{I}_2 + 3 \text{ H}_2\text{O} + 2 \text{ KCI}$
- $\textbf{9} \quad 2 \; \text{Na}_2 \text{S}_2 \text{O}_3 + \text{I}_2 \; \rightarrow \; 2 \; \text{Nal} + \text{Na}_2 \text{S}_4 \text{O}_6$

 $n(\text{Na}_2\text{S}_2\text{O}_3) = 0.200 \text{ mol } \text{dm}^{-3} \times 0.021 \text{ dm}^3 = 4.20 \cdot 10^{-3} \text{ mol}$   $n(\text{I}_2) = 2.10 \cdot 10^{-3} \text{ mol}$   $n(\text{Co}^{2^*}) = 4.20 \cdot 10^{-3} \text{ mol}$   $m(\text{Co}) = 4.20 \cdot 10^{-3} \text{ mol} \times 58.93 \text{ g mol}^{-1} = 0.2475 \text{ g}$ % Co by mass =  $\frac{0.2475 \text{ g}}{0.7934 \text{ g}} \times 100 = 31.2$ 

- **10** Assuming 100 g of complex, there is 13.6 g unaccounted. for molar ratio of  $n(\text{Co}): n(\text{NH}_3): n(\text{Cl}) = \frac{31.2}{58.93}: \frac{27.1}{17.034}: \frac{28.1}{35.453} = 0.529:1.591:0.7926 = 2:6:3.$ Missing species is either O<sup>2-</sup>, OH<sup>-</sup> or H<sub>2</sub>O with similar molar mass ≈ 17 g mol<sup>-1</sup>. Molar fraction of missing oxygen species ≈ 13.6 / 17 = 0.8 i.e. the same as the Cl. Considering charge balance, 2(+3) + 6(0) + 3(-1) = +3, it is needed -3 to balance i.e. the missing species must be OH<sup>-</sup>.
- 11 Empirical formula of H: Co<sub>2</sub> N<sub>6</sub> H<sub>21</sub> O<sub>3</sub> Cl<sub>3</sub>
- 12 Structure must fit the empirical formula worked out above, contain only octahedral cobalt, and be chiral. Some marks deducted if chloride is directly coordinated to cobalt, or if any single ammonia molecule is coordinated to more than one cobalt atom.



(International Chemistry Olympiad, 2019, Preparatory problem 5)

- 1.  $PV = nRT \Leftrightarrow \frac{P}{RT} = \frac{\rho}{M}$  $\rho = \frac{MP}{RT} = \frac{2.0 \cdot 10^{-3} \times 500 \cdot 10^{5}}{8.314 \times 293} = 41.1 \text{ kg m}^{-3}$
- 2. <u>Correct statements:</u> 16 K, 25 K
- 3. Using the Clausius-Clapeyron relation and the boiling point under a pressure of 1 atm:  $\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{\text{vap}}H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right), \text{ so: } P_{27.15\text{K}} = P_{\text{atm}} \exp\left[\frac{\Delta_{\text{vap}}H^\circ}{R} \left(\frac{1}{T_p} - \frac{1}{T_{27.15\text{K}}}\right)\right]$

$$\Delta_{\text{vap}}H^{\circ}_{\text{m}} = 448.69 \text{ kJ kg}^{-1}$$
, so that  $\Delta_{\text{vap}}H^{\circ} = 897.38 \text{ J mol}^{-1}$   
 $P_{27.15\text{K}} = 1.0 \cdot 10^5 \exp\left[\frac{897.38}{8.314} \left(\frac{1}{20.37} - \frac{1}{27.15}\right)\right] = 0.380 \text{ MPa} = 3.75 \text{ atm}$ 

4. Dehydrogenated complex:  $W(CO)_3(P(iPr)_3)_2 = WC_{21}O_3P_2H_{42}$   $M = 588.4 \text{ g mol}^{-1}$ Each complex can store one molecule of dihydrogen. In 1 kg of dihydrogen, there are 500 mol of dihydrogen. Hence, m = 294.2 kg of dehydrogenated complex are needed to store 1 kg of dihydrogen.

Once bound to 1 kg of H<sub>2</sub>, the complex thus weighs  $m_{Kubas} = 295.2$  kg

$$\rho_{\rm H} = \frac{m_{\rm H} \rho_{\rm Kubas}}{m_{\rm Kubas}} \quad \text{hence} \quad \rho_{\rm H} = 6.6 \cdot 10^{-6} \,\text{kg(H_2)} \,\text{m}^{-3}$$

5. [Xe] (6s)<sup>2</sup>(4f)<sup>14</sup>(5d)<sup>4</sup> so 6 valence electrons (4f layer is full)







00

хz

(iPr

- 9. An orbital is symmetric with respect to a symmetry element if it remains the same when the symmetry operation is applied. An orbital is antisymmetric with respect to a symmetry element if it changes to its opposite when the symmetry operation is applied. The results are gathered in the diagram below.
- 10. As a general rule, interactions between two orbitals implying two electrons with the same symmetry lead to a stabilization inversely proportional to the difference of energy between the two orbitals. On the contrary, an interaction between two orbitals implying four electrons destabilizes the complex. Two orbitals have the same symmetry if all the symmetry elements are the same for each of the fragments. Moreover, all valence electrons have to be considered for tungsten to fill the d orbitals. Thus, 6 electrons for the metallic core and 2 electrons for hydrogen molecules are considered. One has to use Aufbau and Pauli principles. The result is depicted on the diagram below.

11. For all conformations,  $d_{z^2}$  and  $d_{x^2-y^2}$  interacts with  $\sigma$ H<sub>2</sub>. For conformation (1), only  $d_{xz}$  interacts with  $\sigma$ \*H<sub>2</sub>. For conformation (2), only  $d_{yz}$  interacts with  $\sigma$ \*H<sub>2</sub>.



In conformation (1),  $\sigma^*$  is SA (symmetric for xz plane and antisymmetric for yz plane) and in conformation (2),  $\sigma^*$  is AS. So in conformation (1),  $\sigma^*$  interacts with  $d_{xz}$  (same symmetry SA), while in conformation (2) it interacts with  $d_{yz}$ . In conformation (1), the energies of the two interacting parts are the closest, thus leading to an enhanced stabilization.

12. 
$$\rho_{\rm H} = \frac{m_{\rm H}}{v} = \frac{n_{\rm H}M_{\rm H}}{v} = \frac{2n_{\rm HCOOH}M_{\rm H}}{v} = \frac{2m_{\rm HCOOH}M_{\rm H}}{M_{\rm HCOOH}v} = \frac{2\rho_{\rm HCOOH}M_{\rm H}}{M_{\rm HCOOH}}$$
  
 $\rho_{\rm H} = \frac{2 \times 1.22.10^3}{(2+12+32)} = 53.0 \text{ kg m}^{-3}$ 

The hydrogen density is higher in formic acid than for high pressure (500 bars) dihydrogen (31 kg m<sup>-3</sup>) but lower than for cryogenic liquid hydrogen (70.85 kg m<sup>-3</sup>). If one can extract efficiently  $H_2$  molecule from formic acid, it constitutes a good alternative to pure  $H_2$  storage.

13.

$$\Delta_{\rm r} H^{\circ} = \sum_{i=1}^{N} \nu_i \Delta_{\rm f} H_i^{\circ}$$
  
$$\Delta_{\rm r} H^{\circ} = -(-425.09) + (-393.51) + 0 = 31.58 \text{ kJ mol}^{-1}$$
  
$$\Delta_{\rm r} S^{\circ} = \sum_{i=1}^{N} \nu_i S_{i,{\rm m}}^{\circ}$$
  
$$\Delta_{\rm r} S^{\circ} = -(131.84) + 213.79 + 130.68 = 212.63 \text{ J mol}^{-1} \text{ K}^{-1}$$
  
$$\Delta_{\rm r} G^{\circ}({\rm T}) = \Delta_{\rm r} H^{\circ} - {\rm T} \cdot \Delta_{\rm r} S^{\circ}$$
  
$$\Delta_{\rm r} G^{\circ}({\rm T}) = 31.58 - 0.213 \times 293 = -30.8 \text{ kJ mol}^{-1}$$

14. 
$$\Delta_r G^{\circ}(T) = \Delta_r H^{\circ} - T \cdot \Delta_r S^{\circ}$$
  
 $\Delta_r G^{\circ}(T) = 31.58 - 0.213 \times 293 = -30.8 \text{ kJ mol}^{-3}$   
 $K^{\circ} = e^{-\frac{\Delta_r G^{\circ}}{RT}}$   
So:  $K^{\circ} = 3.1 \cdot 10^5$ 

15. 
$$n_{N_2} = n_{N_2,0} = \frac{PV}{RT}$$
  
 $n_{N_2} = \frac{1.013.10^5 \times 1.0.10^{-3}}{8.314 \times 298.15} = 0.04 \text{ mol}$ 

	HCOOH(l)	CO <sub>2</sub> (g)	H <sub>2</sub> (g)
Initial	n <sub>HCOOH</sub>	$n_{\rm CO_{2,0}}$	$n_{\mathrm{H}_{2,0}}$
Intermediate	$n_{ m HCOOH} - \xi$	$n_{\mathrm{CO}_{2,0}} + \xi$	$n_{\mathrm{H}_{2},0}+\xi$
Final	0	$n_{\rm CO_{2,0}} + n_{\rm HCOOH}$	$n_{\rm H_{2},0} + n_{\rm HCOOH}$

 $n_{\text{H}_2,0} = 0$  mol, so at equilibrium:  $n_{\text{CO}_2} = n_{\text{H}_2} = n_{\text{HCOOH},0}$ 

16. LaNi<sub>5</sub>H<sub>6</sub>:  $\rho_{\rm H} = 118 \text{ kg m}^{-3}$ Mg<sub>2</sub>NiH<sub>4</sub>:  $\rho_{\rm H} = 95 \text{ kg m}^{-3}$ 

## **Problem 20 (Practical)**

(International Chemistry Olympiad, 2001, Problem 3)

Concentration of standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>: 0.010 M

Concentration of  $HCrO_4$  at t = 0 : 0.0074 M

	Titration 1	Titration 2	Titration 3	Titration 4
	[10 mins.]	[20 mins.]	[30 mins.]	[40 mins.]
Initial burette reading (mL)	00.0 mL	00.0 mL	00.0 mL	00.0 mL
Final burette reading (mL)	16.4 mL	12.2 mL	9.0 mL	6.8 mL
Volume of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (mL)	16.4 mL	12.2 mL	9.0 mL	6.8 mL

Acetic acid	CH <sub>3</sub> COOH
Acetaldehyde	CH <sub>3</sub> CHO

2 HCrO<sub>4</sub><sup>-</sup> + 6l<sup>-</sup> + 14 H<sup>+</sup>  $\rightarrow$  3 l<sub>2</sub> + 2Cr<sup>3+</sup> + 8H<sub>2</sub>O

 $\mathsf{I_2} + 2 \; \mathsf{S_2O_3} \; {}^{2\text{-}} \rightarrow \; 2 \; \mathsf{I^-} + \; \mathsf{S_4O_6}^{2\text{-}}$ 

[S<sub>2</sub>O<sub>3</sub><sup>2-</sup>] x Vs<sub>2</sub>O<sub>3</sub><sup>2-</sup> = 3 [HCrO<sub>4</sub><sup>-</sup>] x Vнсrо<sub>4</sub><sup>-</sup> 0.010 x 6.8 = 3 [HCrO<sub>4</sub><sup>-</sup>] x 10.0 [HCrO<sub>4</sub><sup>-</sup>] = 0.0027

Time (mins.)	[HCrO₄⁻]	In [ HCrO₄⁻]
0	0.0074	-4.906
10	0.0056	-5.185
20	0.0041	-5.497
30	0.0030	-5.809
40	0.0027	-5.914

**x** = 1

$k = 0.026 \text{ mm}^{-1}$
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#### **Problem 21 (Practical)**

(International Chemistry Olympiad, 2021, Preparatory problem 2)

- 1. NaOH + HCl  $\rightarrow$  NaCl + H<sub>2</sub>O Na<sub>2</sub>CO<sub>3</sub> + HCl  $\rightarrow$  NaCl + NaHCO<sub>3</sub>
- 2. NaHCO<sub>3</sub> + HCl  $\rightarrow$  NaCl + H<sub>2</sub>O + CO<sub>2</sub>
- 3. NaOH [g] :  $0.0040 \times (V_a V_b) / \frac{20}{1000}$  [g]

$$Na_2CO_3$$
 [g] :  $0.0053 \times 2 \times (V_b) / \frac{20}{1000}$  [g]

4. The horizontal axis is the amount of the standard solution added, while the vertical axis is the pH value of the unknown alkali solution. The following figure shows the actual measurement data (unknown alkali solution: 30.00 mL) where the unknown alkali solution was prepared from 1.0 L distilled water containing 0.5 g of NaOH and 2.5 g of Na<sub>2</sub>CO<sub>3</sub>.



#### **Problem 22 (Practical)**

(International Chemistry Olympiad, 2013, Preparatory problem 30)

1. Titration curves for a polyprotic acid (such as phosphoric acid) or a mixture of acids are characterized by more than one endpoint if  $K_{a1}:K_{a2} \ge 10^4$  and the equilibrium constant of acidity of the weak acid is more than  $n \times 10^{-9}$ . The equilibrium constants of acidity of phosphoric acid are:  $K_{a1} = 7.1 \times 10^{-3}$ ,  $K_{a2} = 6.2 \times 10^{-8}$ ,  $K_{a3} = 5.0 \times 10^{-13}$ . Thus, there are two breaks on the titration curve of phosphoric acid (Fig. 1). The third break is not observed due to very low value of  $K_{a3}$ .



Fig. 1. Titration of a mixture of hydrochloric and phosphoric acids with sodium hydroxide.

During titration of a *mixture* of hydrochloric and phosphoric acids, the proton of hydrochloric acid and the first proton of phosphoric acid react with sodium hydroxide simultaneously. By the second endpoint  $H_2PO_4^-$  is converted into  $HPO_4^{2^-}$ .

- 2. The first and second equivalence points of  $H_3PO_4$  are observed at pH of about 4.7 and 9.6, respectively. For determination of hydrochloric and phosphoric acids in their mixture, one can use indicators with color change around these pH values (for example, bromocresol green and thymol phthalein for the first and second titrations, respectively).
- 3. The following reaction takes place on addition of HCl to the sample:

$$(NH_4)_2HPO_4 + 2HCl = 2NH_4Cl + H_3PO_4$$

Formaldehyde reacts with ammonium salts to form hexamethylene tetrammonium cation:

$$4NH_4^+ + 6H_2CO = (CH_2)_6(NH^+)_4 + 6H_2O$$

The equations describing the titration of hexamethylene tetrammonium salt, hydrochloric and phosphoric acids with sodium hydroxide:

$$(CH_2)_6(NH^+)_4 + 4OH^- = (CH_2)_6N_4 + 4H_2O$$
$$HCl + NaOH = NaCl + H_2O$$
$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

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$$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O$$

**4.** A typical analysis of potentiometric titration data is shown in Fig. 2. The most steeply rising portion on the curve (a) corresponds to the endpoint, which can be found more precisely by studying dependences of the first (maximum on curve (b)) or second (zero value on curve (c)) derivatives. In the presence of ammonium salts, the reaction corresponding to the second end point in  $H_3PO_4$  titration

$$H_2PO_4^- + OH^- = HPO_4^{2-} + H_2O$$

is overlaid by the process

$$\mathbf{NH_4}^+ + \mathbf{OH}^- = \mathbf{NH}_3 + \mathbf{H}_2\mathbf{O}$$

which makes the potential rise gradually rather than sharply (ammonium buffer).



Fig. 2. Typical plots of potentiometric titration:

- a) Titration curve of an acid by base;
- b) Curve of the furst derivative;
- c) Curve of the second derivative.

5.

#### (a) Calculation of phosphate amount

With  $V_{\text{NaOH},1}$  designating the volume of sodium hydroxide used in titration **A**, the amount needed to neutralize hydrochloric acid and the first proton of phosphoric acid is:

$$n_{\rm PO4} + n_{\rm HCl} \text{ (titrated)} = c_{\rm NaOH} \times V_{\rm NaOH,1}$$

At the same time,

 $c_{\rm HCl} \times V_{\rm HCl}$  (added) =  $n_{\rm HCl}$  (titrated) +  $2n_{\rm PO4}$  (HCl spent for the reaction with (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>) Then,

 $n_{\rm PO4} = c_{\rm HC1} \times V_{\rm HC1} (\rm added) - c_{\rm NaOH} \times V_{\rm NaOH,1}$ 

Since  $n_{(NH4)2HPO4} = n_{PO4}$ , one finally gets:

 $\omega_{\text{(NH4)2HPO4}} = 10 \times n_{\text{PO4}} \times M_{\text{(NH4)2HPO4}} / m_{\text{mixture}}$ 

(b) Calculation of the total amount of diammonium hydrophosphate and ammonium chloride

With  $V_{\text{NaOH},2}$  designating the volume of sodium hydroxide used in titration **B** (that is, spent for the neutralization of hexamethylene tetrammonium cation  $(\text{CH}_2)_6(\text{NH}^+)_4$  obtained from the ammonium salts), one gets:

$$n_{\rm NH4Cl} + 2n_{\rm PO4} = c_{\rm NaOH} \times V_{\rm NaOH,2}$$

The amount of phosphate  $n_{(NH4)2H3PO4}$  was determined in experiment **A**, which allows calculating the amount of NH<sub>4</sub>Cl

 $n_{\text{NH4Cl}} = c_{\text{NaOH}} \times V_{\text{NaOH},2} - 2 \cdot (c_{\text{HCl}} \times V_{\text{HCl}} - c_{\text{NaOH}} \times V_{\text{NaOH},1})$ 

and its content in the mixture:

 $\omega_{NH4Cl} = 10 \times n_{NH4Cl} \times M_{NH4Cl} / m_{mixture}$ 

#### Problem 23 (Practical)

(International Mendeleev Chemistry Olympiad, 2018, Problem 2)

**3.** In the most acidic medium (a), since there would be some OH-groups unreacted with the acid left at higher pH values. (Here we imply the conditions of the titration carried out by the participants: the pH value given in the question is the final one).

**4.**  $Al(OH)_3 + H^+ = Al(OH)_2^+ + H_2O$ 

$$Al(OH)_{2}^{+} + H^{+} = Al(OH)^{2+} + H_{2}O$$

 $Al(OH)^{2+} + H^{+} = Al^{3+} + H_2O$ 

At higher acidity all the reactions proceed to a greater conversion degree. At pH 3– 4 the equilibria are shifted leftwards. Any of the total equations is sufficient.

*Note*. On the contrary, magnesium hydroxide enters the reaction at weakly acidic medium, even at pH 4.