11th BALTIC CHEMISTRY OLYMPIAD

RIGA, APRIL 25-27, 2003
SOLUTIONS

PROBLEM 1

Percentage of space occupied by spheres in the *fcc* arrangement:

$(4 \cdot 4/3 \cdot \pi r^3)/(4 \cdot r/(2^{1/2}))^3 = \pi/(3 \cdot (2^{1/2})) = 0.740$

Total volume of the layer formed by 1 mol of peas:

$V = (6{,}02 \cdot 10^{23} \cdot 4/3 \cdot \pi r^3)/0{,}740 = 9.20 \cdot 10^{16}$ m^3

$V = 4/3\, \pi (R_2^3 - R_1^3)$,

where R_2 - the outer radius of the layer of peas,

   R_1 - the inner radius of the layer of peas.

The inner radius R_1 can be calculated from the surface of the Earth:

$R_1 = (S/(4\pi))^{1/2} = 6.370597 \cdot 10^6$ m.

$R_2 = ((V + 4/3\, \pi\, R_1^3)/(4/3\, \pi))^{1/3} = 6.370777 \cdot 10^6$ m.

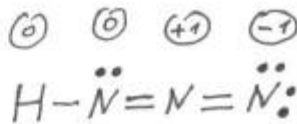The thickness of the layer $d = R_2 - R_1 = 180$ m.

The correct answer is **b.**

Lupine would fit into the octahedral holes, which can accommodate particles with the diameter up to $0.414 \cdot 6 = 2.5$ mm.
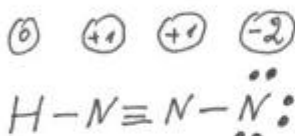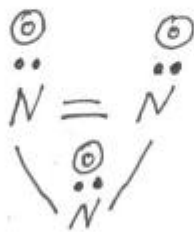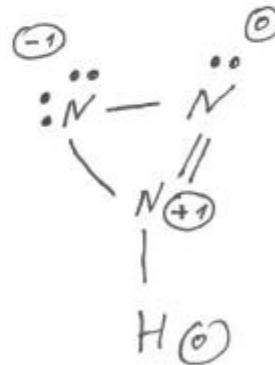
PROBLEM 2

   i)

ii) structures **A** and **B**

iii) angle H–N–N   between 120° and 109°   angle N–N–N   180°

iv)

$$sp^2 \quad sp \quad sp^2$$
$$N = N = N$$
$$/$$
$$H$$

$$sp^3 \quad sp \quad sp$$
$$N — N \equiv N$$
$$/$$
$$H$$
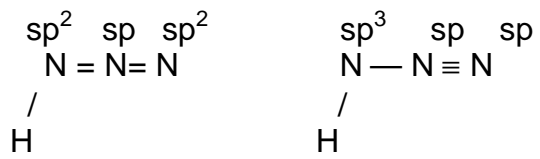
v) $\Delta H_f° = 622 + 2(-285,8) = 50,4$ kJ/mol

Actual structure
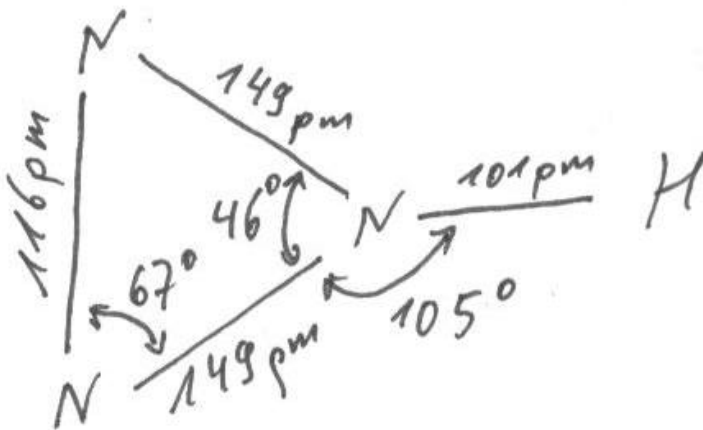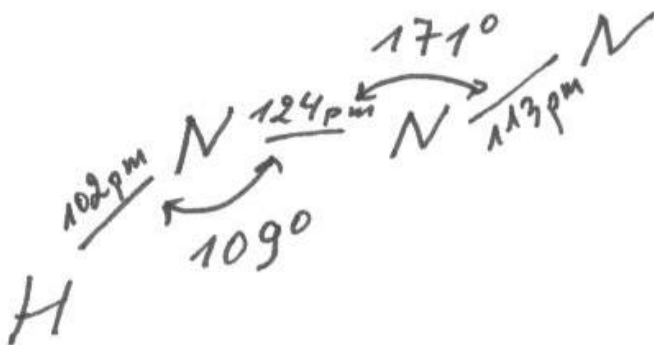
PROBLEM 3

a) $n(^4_2He) = (226 - 206) \cdot 4 = 5$

$n(\beta) = 5 \cdot 2 - (88 - 82) = 4$

b) $v = k \cdot c$; $\tau = \dfrac{\ln 2}{k}$

$v_1 = v_2$

$k_1 \cdot c_1 = k_2 \cdot c_2$

$\dfrac{k_2}{k_1} = \dfrac{c_1}{c_2}$

$\dfrac{\tau_1}{\tau_2} = \dfrac{k_2}{k_1} = \dfrac{c_1}{c_2} \Leftrightarrow \dfrac{n_1}{n_2}$

c) $c \Leftrightarrow n$

$n = \dfrac{m}{M}$

$\dfrac{1580 \text{ year} \cdot 365{,}25 \text{ day / year}}{138{,}8 \text{ day}} = \dfrac{m(Ra)}{226 \text{ g / mol}} \cdot \dfrac{210 \text{ g/mol}}{10^{-3} \text{ g}}$

$m(Ra) = \dfrac{1580 \text{ year} \cdot 365{,}25 \text{ day / year}}{138{,}8 \text{ day}} \cdot \dfrac{10^{-3} \text{ g}}{210 \text{ g / mol}} \cdot 226 \text{ g / mol} = 4{,}47 \text{ g}$

$m(ore) = 4{,}47 \text{ g} \cdot \dfrac{1 \text{ t}}{0{,}14 \text{ g}} = 31{,}9 \text{ t} \approx 32 \text{ t}$

d) $^{226}_{88}Ra = {}^{210}_{84}Po + 4\alpha + 4\beta$

$\Delta m = 4 \cdot 0{,}00055 \text{ u} + 4 \cdot 4{,}00273 \text{ u} + 209{,}98286 \text{ u} - 226{,}0254 \text{ u} = -0{,}02942 \text{ u}$

e) $\Delta m = \dfrac{10^{-3} \text{ g}}{210 \text{ g / mol}} \cdot 0{,}02942 \text{ u} \cdot 1 \text{ g/mol·u} = -1{,}40 \cdot 10^{-7} \text{ g}$

$\Delta E = -1{,}40 \cdot 10^{-10} \text{ kg} \cdot 9{,}0 \cdot 10^{16} \text{ m}^2/\text{s}^2 = -1{,}26 \cdot 10^7 \text{ J} = -1{,}26 \cdot 10^4 \text{ kJ} \approx -1{,}3 \cdot 10^4 \text{ kJ}$

PROBLEM 4

a) For the reaction (1) $\qquad E_1 = E^o(Ag^+/Ag) + \dfrac{RT}{F} \cdot \ln c(Ag^+)$

For the reaction (2) $\qquad E_2 = E^o(I^-/AgI/Ag) - \dfrac{RT}{F} \cdot \ln c(I^-)$

The equilibria are established on the same electrode, therefore $E_1 = E_2$

$E^o(Ag^+/Ag) - E^o(I^-/AgI/Ag) = -\dfrac{RT}{F} \ln\left[c(Ag^+) \cdot c(J^-)\right]$

The solubility product $L = c(Ag^+) \cdot c(I^-)$

$$\log L = \frac{-0,152 - 0,799}{0,0591} = -16,091 \qquad \mathbf{L = 8,13 \times 10^{-17}}$$

b) $Ag(s) + H^+ (sol) \Leftrightarrow Ag+(sol) + 0.5\ H_2\ (g)$ (3)
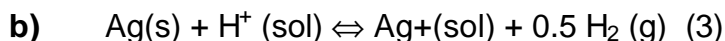
$0,799 + 0,0591 \cdot \lg c(Ag^+) = 0 + 0,0591 \cdot \lg 1$

$\lg c(Ag^+) = \dfrac{-0,799}{0,0591} = -13,52$

$c(Ag+) = 10^{-13.52}\ mol/dm^3$

As the product of ions concentration in solution $c(Ag^+) \cdot c(I^-) = 10^{-13.52} \cdot 1$
is remarkably higher than the solubility product $8.13 \cdot 10^{-17}$, the AgI   is precipitated, shifting the equilibrium from left to right. Thus, thermodynamically both the dissolution of silver and the evolution of hydrogen are possible.

c) The reaction (3) is hindered by the formation of passivating AgI film and polarization phenomenon due to the H_2 evolution.

PROBLEM 5

1. Amount of selenious acid n = m / M = 1.29 / 129 = 0.01 mol

2. Concentration of solution: c_o = n /v = 0.01 / 0.1 = 0.1 mol/ l

3. Amount of NaOH in each portion (5 ml): n = c.v = 0.005 * 1 = 0.005 mol

4. pH values are determined by protolytic equilibrium in water solution. Different protolytic systems created from selenious acid and hydroxide ions should be analyzed solving this problem. Formulas for calculation of pH in different protolytic systems may be memorized or derived from corresponding chemical equilibria.

No.	Total volume of NaOH added, mL	Equation of reaction	Formula for calculation of pH (see for comments below)	Calculated pH value
1.	0	$H_2SeO_3 + H_2O =$ $HSeO_3^- + H_3O^+$	(weak acid in water) $pH = \frac{1}{2}\ (pK_1 - \lg c_A)$	1.81
2.	5.00	$H_2SeO_3 + OH^- \rightarrow$ $HSeO_3^- + H_2O$	(buffer system) $pH = pK_1 + \lg\ (c_B / c_A)$	2.62
3.	10.00	$H_2SeO_3 + OH^- \rightarrow$ $HSeO_3^- + H_2O$	(amphyprotic substance) $pH = \frac{1}{2}\ (pK_1 + pK_2)$	5.47
4.	15.00	$HSeO_3^- + OH^- \rightarrow$ $SeO_3^{2-} + H_2O$	(buffer system) $pH = pK_2 + \lg\ (c_B / c_A)$	8.32
5.	20.00	$HSeO_3^- + OH^- \rightarrow$ $SeO_3^{2-} + H_2O$	(weak base) $pH = \frac{1}{2}\ (14 + pK_2 + \lg c_B)$	10.66
6.	25.00	OH^- (excess)	(strong base) $pH = 14 + \lg c_B$	12.70

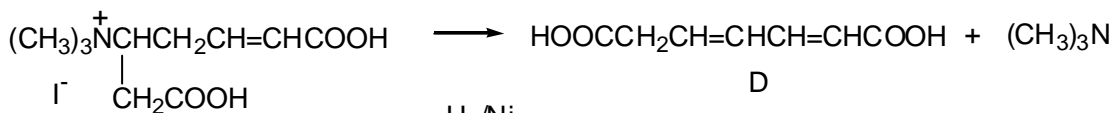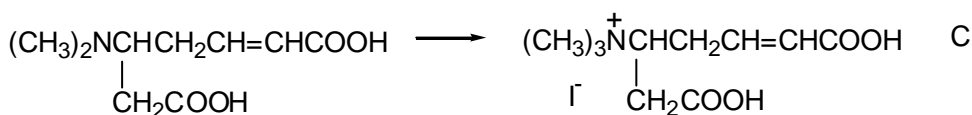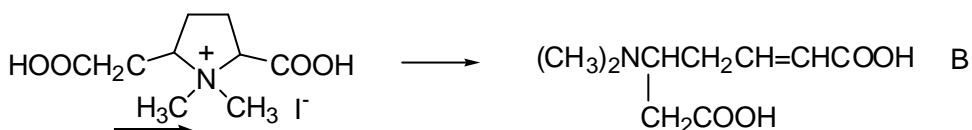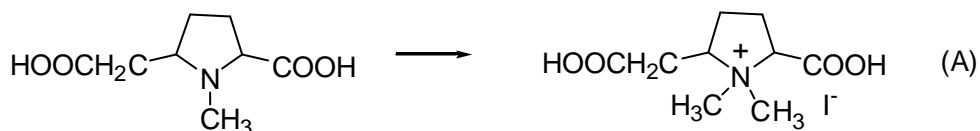**Comments.**

1. Concentration of protolytes determining pH values(mol/l): 1) H_2SeO_3 0.1; 2) H_2SeO_3 0.05, $HSeO_3^-$ 0.05; 3) $HSeO_3^-$ 0.1; 4) $HSeO_3^-$ 0.05, SeO_3^{2-} 0.05; 5) SeO_3^{2-} 0.1; 6) excess of OH^- 0.05.

2. If changes in solution volume was taken in consideration, calculated pH values **are slightly different.**

PROBLEM 6

The reaction schemes indicated *a-e* are as follows:
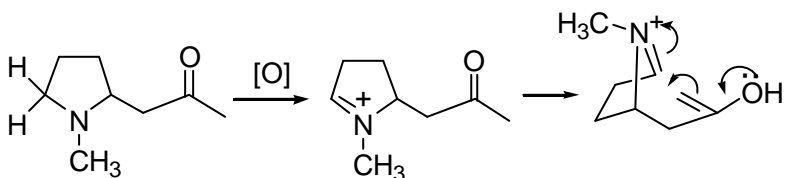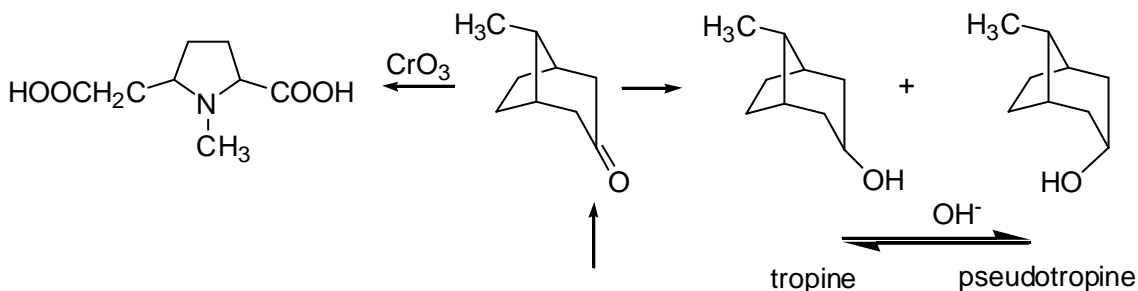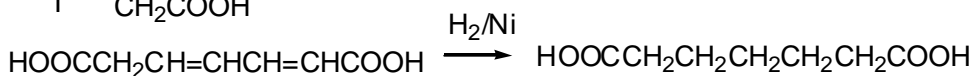
Oxidation of tropinone leads to ring reopening.

Reduction of tropinone gives two isomeric alcohols, namely tropine and pseudotropine, which differ in *exo-* or *endo-*position of hydroxyl group. The first is converted to tropine under basic conditions.

Sythesis of tropinone from hygrine is shown in the last sheme. Oxidation leads to hydrogen abstraction with subsequent enolization of ketone and the following cyclization.