Baltic Chemistry Competition

BioSan
Medical - Biological Research and Technologies
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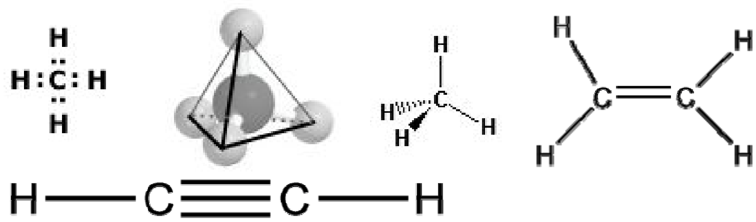
2011

2ND ROUND, SOLUTIONS

Problem 1 (Lithuania)

If you do not knw – ask google! (5 points)

1. sp2, sp3, sp hybridization More information: http://en.wikipedia.org/wiki/Carbon_allotropes
   sp^2 – ethane; sp^3 – methane; sp – ethyne
   Lewis structures:



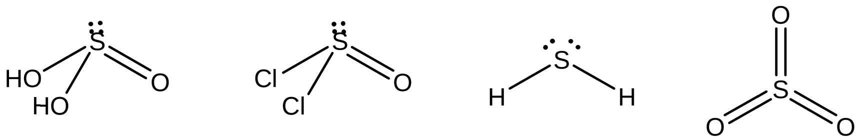
2. a – diamond (sp^3), b – graphite (sp^2), c – lonsdaleite (sp^3)
3. Heating organic materials, they decomposes forming amorphous carbon and water or other gaseous compounds.
4. Amorphous carbon. Amorphous carbon materials may also be stabilized by terminating dangling-π bonds with hydrogen. These materials are then called hydrogenated amorphous carbon.
5. Fullerene. The remaining electrons are delocalized over the molecule (or a part of it) in pi-bonding orbitals. These electrons are the “valence shell” of the molecule and therefore it attempts to fill the shell. Usually, fullerenes react as electrophiles; also, they can be hydrogenated plus fullerenes also have superconductor properties.
6. Carbon nanotube.
7. Agregated diamond nanoroads (ADNR) or fullerite.
   http://en.wikipedia.org/wiki/Aggregated_diamond_nanorod
8. Diamonds are thermodynamically unstable but kinetically stable (metastable modification of carbon). Transformation is thermodynamically possible but transformation rate is to slow (not enough activation energy). Heating of diamond at anaerobic conditions it transforms to amorphous carbon (at temperatures aprox. 1000^{o}C). At aerobic conditions it oxidizes and forms carbon dioxide.
   Liquid carbon cannot exist at normal pressure, sublimation is observed.
9. It is graphene. Hybridization is sp^2.
10. Carbon fibre / modified graphite. The carbon form is graphene (one-sheet thick graphite) and it forms carbon fiber. Carbon fiber is very strong while bending, compared to its weight, but will easily break if compressed or exposed to shock (hit with hammer).

Each question was graded with max 0.5 points.

Problem 2 (Estonia)

Compounds of sulfur (5 points)

Google translated english: Väävli ühendid



a) .

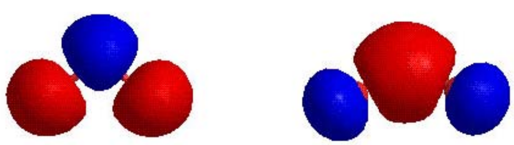
Polar polar polar

b) Compared to O-O pi-bonds, S-S pi-bonds are much weaker. Therefore, oxygen accounts for two- and three-membered molecules, but sulphur forms long chains containing sigma-bonds.

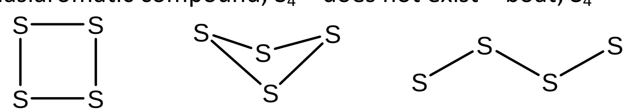
c) SO_2 molecule contains double bonds, O_3 has 1,5-bonds. Common Lewis structures are:

Lewis structure provide a few information and actually are wrong. In SO_2 molecule there are four bonding MOs, which are formed from AOs: p_z-p_z-p_z (π_2), p_y-p_y-p_y (π_1), p_x-p_x-p_x (σ_2), p_x-s-p_x (σ_1); In O_3 only three: p_z-p_z-p_z (π_2), p_y-p_y-p_y (π_1), p_x-p_x-p_x (σ_2), π_2 and π_1 has almost the same energy. In O_3 molecule p_x-s-p_x MO is non-bonding due to the low energy of oxygen s-AO and shielding effect of s-s-s MO.

O_3 SO_2



d) S_4^{2+} – planar, is quasiaromatic compound; S_4 – does not exist – boat; S_4^{2-} – a chain.



e) SF_6 is strongly shielded.

Problem 3 (Lithuania)

Quantum observations due to laser cooling (10 points)

1. ^{87}Rb atom has 87 nucleons and 37 electrons, hence: 87 + 37 = 124 subatomic particles in total, and 124 is even. ^{23}Na has 23 nucleons and 11 electrons- 34 subatomic particles. The number of electrons is equal to the number of protons in an atom, so it actually only depends on the number of neutrons- if it is even, then the atom is a boson.
2. Two lasers in every possible dimension, therefore 6 lasers in 3D.
3. The general equation is: $E_k = \frac{f}{2}\mathrm{kT}$, where f is the number of degrees of freedom and for monatomic gas it is 3. As we can see, the kinetic energy only depends on the type of the gas. Because both sodium and rubidium gasses are monatomic their average kinetic energies are equal: $E_k = \frac{3}{2}\mathrm{kT} = 1.5 * 1.380 * 10^{-23}\mathrm{J/K} * (25.00 + 273.15)K = 6.172 * 10^{-21}\mathrm{J}$
4. $v = \sqrt{\frac{3\mathrm{RT}}{M}} = \sqrt{\frac{3*8.314\frac{J}{mol*K}*170.0*10^{\wedge}(-9)K}{87.00*10^{\wedge}(-3)\frac{kg}{mol}}} = 6.981 \times 10^{-3}\,\frac{m}{s} = 6.981\,\frac{mm}{s}$
5. $E = \frac{\mathrm{hc}}{\lambda} = \frac{6.626*10^{-34}\ \mathrm{Js}\ *2.99\ 8*10^{8}\frac{\boldsymbol{m}}{\boldsymbol{s}}}{780.0*10^{-9}\mathrm{m}} = 2.54676 * 10^{-19}\,J$
6. This energy corresponds to the energy needed for the electron of rubidium to go from the s orbital of the fifth layer to the p orbital of the same layer: $5s^1 \rightarrow 5p^1$
7. The general Doppler effect is expressed in the following way for the moving detector (atom) and stationary source (laser):

$$f' = f\,\frac{\mathrm{v} \pm v_{\mathrm{d}}}{\mathrm{v}}$$

Where f' is the frequency observed by the detector and f is the frequency of the source. If we put f'=f(atom), f= f(laser), v= c, v(d)= v(atom) then:

$$f_{\mathrm{atom}} = f_{\mathrm{laser}}\frac{\mathrm{c} \pm v_{\mathrm{atom}}}{\mathrm{c}} = f_{\mathrm{laser}}(1 \pm \frac{v_{\mathrm{atom}}}{\mathrm{c}})$$

Because we want for the atoms to slow down when they are moving towards the laser, so the frequency detected by the atom increases. So we take v/c positive. If we then divide by$\left(1 + \frac{v_{\mathrm{atom}}}{\mathrm{c}}\right)$ we obtain the desired equation

$$f_{\mathrm{laser}} = \frac{f_{\mathrm{atom}}}{\left(1 + \frac{v_{\mathrm{atom}}}{\mathrm{c}}\right)}$$

Due to the fact that the speed of the atoms is really small, compared to the speed of light, we do not have to take the relativity into account.

8. $\Delta f_{atom} = \frac{v_{\mathrm{atom}}}{c} f_{\mathrm{laser}} = \frac{v_{\mathrm{atom}}*c}{c*\lambda} = \frac{\sqrt{\frac{3\mathrm{RT}}{M}}}{\lambda} = \frac{\sqrt{\frac{3*8.314*(25.00+273.15)}{87*10^{-3}}}}{780.0*10^{-9}} =$ $3.748 \times 10^{8} Hz$

Compared to the 3.846×10^{14} Hz frequency of thelaser it is not a lot, so during the experiments the scientists usually detune the lasers using the trial and error method.

Problem 4 (Latvia)

Chemistry of green compounds (5 points)

① 31,7 mg ⇒ CuO
19,7 mg ⇒ $BaCO_3$

malachite
$(CuOH)_2CO_3$
↓ t°
$2CuO + H_2O + CO_2\uparrow$ (1)

$n_{CuO} = \frac{m}{M} = 0,40$ mmol

$n_{CO_2} = n_{BaCO_3} = \frac{19,7}{197} = 0,1$ mmol

$n_{malachite} = \frac{m}{M} = \frac{88,5}{222} = 0,40$ mmol ⇒ half ⇒ 0,20 mmol

$n_{CO_2} = 0,2$ mmol (according to equation (1))

$n_{CuO} = 0,4$ mmol ⇒ ERROR IN PROBLEM

accepted answers $(CuOH)_2CO_3$ – malachite
or $2CuO \cdot H_2O \cdot CO_2$
↓

$n_{CuO} : n_{CO_2 (observed)} : n_{H_2O} = 0,40 : 0,10 : n_{H_2O}$

$n_{H_2O} = ?$

$m_{CO_2} = 0,10 \cdot 44 = 4,4$ mg $m_{H_2O} = \frac{88,5}{2} - 4,4 - 31,7 = 8,15$ mg

$n_{H_2O} = \frac{8,15}{18} = 0,45$ mmol

$n_{CuO} : n_{CO_2} : n_{H_2O} = 0,4 : 0,1 : 0,45$

② red – oxygen
pink – copper
white – hydrogen
grey – carbon

③ using geometry rules or appropriate programs such as Full Prof software (Winplotr) calculate volume of unit cell:

$$V = 364{,}4\ \text{Å}^3$$

mass of one malachite formula unit

$$m_0 = \frac{M}{N_A} = \frac{222}{6{,}02\cdot 10^{23}} = 3{,}7\cdot 10^{-22}\ g$$

unit cell contains 4 "molecules" of malachite (Z = 4)

$$\rho = \frac{m_0 \cdot Z}{V} = \underline{4{,}05\ g/cm^3}$$

④ ERROR IN PROBLEM ⇒ it should be 61,3 mg and 10.1 mg

$$n_{CuO} = \frac{m}{M} = \frac{61{,}3}{80} = 0{,}766\ mmol$$

$$n_{CO_2} = n_{BaCO_3} = \frac{10{,}1}{197} = 0{,}051\ mmol$$

$$n_{CuO} : n_{CO_2} = 1{,}5 : 1 = 3 : 2$$

$$m_{H_2O} = ?$$

it is not possible to calculate from data given

it should be azurite

$Cu_3((OH)CO_3)_2$

$3CuO \cdot H_2O \cdot 2CO_2$

⑤ $V_{unit\ cell} = 303{,}37\ \text{Å}^3$

ERROR IN PROBLEM → ⇒ IT SHOULD BE compound B

$Z = 2$ $M = 344{,}67\ g/mol$

$$\rho = \frac{344{,}67 \cdot 2}{6{,}02\cdot 10^{23} \cdot 303{,}37\cdot 10^{-24}} = \underline{3{,}77\ g/cm^3}$$

⑥ element C is copper

$$Cu_3((OH)CO_3)_2 \xrightarrow{t^\circ} 3CuO + CO_2\uparrow + H_2O$$

CuO + reducing agent → Cu + oxidation product

reducing agent: C, CO, H_2; oxidation product: CO, CO_2, H_2O

⑦ e. pseudopolymorph

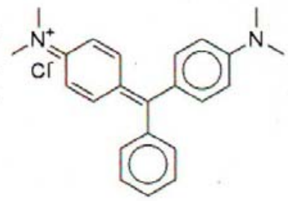
8. Condensation:

$C_6H_5CHO + 2\ C_6H_5N(CH_3)_2 \rightarrow C_6H_5CH(C_6H_4N(CH_3)_2)_2 + H_2O$

Oxidation in acidic environment:
$C_6H_5CH(C_6H_4N(CH_3)_2)_2 + HCl + MnO_2 \rightarrow [C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl + H_2O + MnO$

It is Malachite green or by IUPAC: 4-[(4-dimethylaminophenyl)phenyl-methyl]-*N*,*N*-dimethylaniline
The compounds are only similar in color, there is no chemical relation.

9. Color occurs because this compound has sufficient extension of conjugated pi-electrons and therefore is able to absorb visible light of particular wavelength.



10. Dye; biological stain for microscopic analysis of cells or tissues; anti-parasite and anti-microbial for freshwater fish
Source: http://www.wetwebmedia.com/malachitegreen.htm ;
http://www.fishdoc.co.uk/treatments/malachite.htm ;
http://en.wikipedia.org/wiki/Malachite_green .

Solutions for questions 8 – 10 coppied from Jurgis Kuliesius (Lithuania).

Each question was graded with max 0.5 points. Questions 1-5 were awarded with maximum points also without complete solution (due to errors in problem text).

Problem 5 (Chemical rebuss)

Chemical rebuss (5 points)

1.

A – NOCl	F – HNO_2	K – HCN
B – HCl	G – H_2SO_4	L – CNCl
C – HNO_3	H – $NOHSO_4$	M – $(CN)_2$
D – NO	I – Cu	N – NO_2
E – Cl_2	J - $Cu(NO_3)_2$	

2.

$$\Delta H_f^0(NOCl_{(g)}) = 51.71 kJ/mol$$

$$\Delta H_f^0(NO_{(g)}) = 90.25 kJ/mol$$

$$S^0(NOCl_{(g)}) = 261.69 J/(mol \cdot K)$$

$$S^0(NO_{(g)}) = 210.761 J/(mol \cdot K)$$

$$S^0(Cl_{2(g)}) = 223.066 J/(mol \cdot K)$$

$$2NOCl_{(g)} \leftrightarrow 2NO_{(g)} + Cl_{2(g)} \quad \Delta H_r^0 = 77.08 kJ/mol \quad \Delta S_r^0 = 121.21 J/(mol \cdot K)$$

$$K = e^{-\frac{\Delta H_r - T\Delta S_r}{RT}} = e^{-\frac{77080 J/mol - 400K \cdot 121.21 J/(mol \cdot K)}{8.314 J/(mol \cdot K) \cdot 400K}} = 1.84 \times 10^{-4}$$

$$K_C = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.84 \times 10^{-4}}{0.008314 \cdot 400} = 5.53 \times 10^{-5}$$

$$[NOCl]_0 = 0.50M$$

$$[Cl_2]_0 = [NO]_0 = 0.00M$$

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{4x^3}{(0.50-2x)^2} = 5.53\times10^{-5}$$

$$4\,x^3 - 0.0002212\,x^2 + 0.0001106\,x - 0.000013825 = 0$$

$$x \approx 0.0145$$

$$[NOCl] = 0.5 - 2\cdot 0.0145 \approx 0.471M$$

$$[NO] = 2\cdot 0.0145 \approx 0.029M$$

$$[Cl_2] \approx 0.0145M$$

3.

$$\chi(NOCl) = \frac{n(NOCl)}{n(NOCl)+n(NO)+n(Cl_2)} = \frac{n(NOCl)}{1.5n(NOCl)_0 - 0.5n(NOCl)} = \frac{p(NOCl)}{1.5p(NOCl)_0 - 0.5p(NOCl)}$$

For example $p(NOCl)_0$=1bar, then:

$$p(NOCl) = 0.0149bar$$

$$p(NO) = 0.985bar$$

$$p(Cl_2) = 0.493bar$$

$$K = K_p = \frac{0.985^2\cdot 0.493}{(0.0149)^2} = 2.15\times10^3$$

$$T = \frac{\Delta H}{\Delta S - R\ln K} = \frac{77080J/mol}{121.21J/(molK) - 8.314J/(molK)\cdot\ln(2.15\times10^3)} = 1343K$$