Baltic Chemistry Competition

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2ND ROUND, SOLUTIONS

Problem 1 (Latvia)

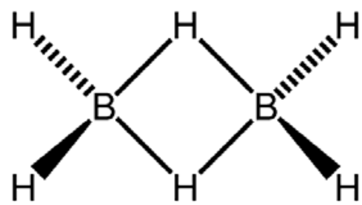
Unknown highly flammable gas (6 points)

Solution

1) Assuming that **A** has a formula EH_x molar mass of element E can be determined.

x	M_E / g mol^{-1}	element E
1	3,6	-
2	7,2	-
3	10,8	Boron
4	14,4	-
5	18,0	-
6	21,6	-

Compound **A** may have the formula BH_3. However, the first reaction equation suggests that **A** is a dimer. Therfore, **A** is diborane B_2H_6. It has the following structure:



Boron atoms are tetrahedral. The interesting feature of this molecule is bonding of the bridging Hydrogens. The B-H-B bond is an example of a 2-electron-3-centre bond.

2)

Letter	Formula
B	BH_3
C	B_3H_9
D	B_3H_7
E	B_4H_{10}
F	B_5H_{11}

3) In monomeric BH_3 Boron atom has got an empty 2p orbital and six electrons (two from each B-H bond). Formation of a dimer allows to fulfil the octet rule as the electrons of the bridging Hydrogens become equally shared between both Boron atoms.

Problem 2 (Latvia)

Chemistry behind ice hockey (14 points)

Solution

1. The length of NHL ice hockey rink is 61 m, width – 26 m, as the ring is rounded rectangle-shaped, we should also consider the size of rounded corners (the radius is 3 m). The area of an NHL ice hockey rink is 61 · 26 –

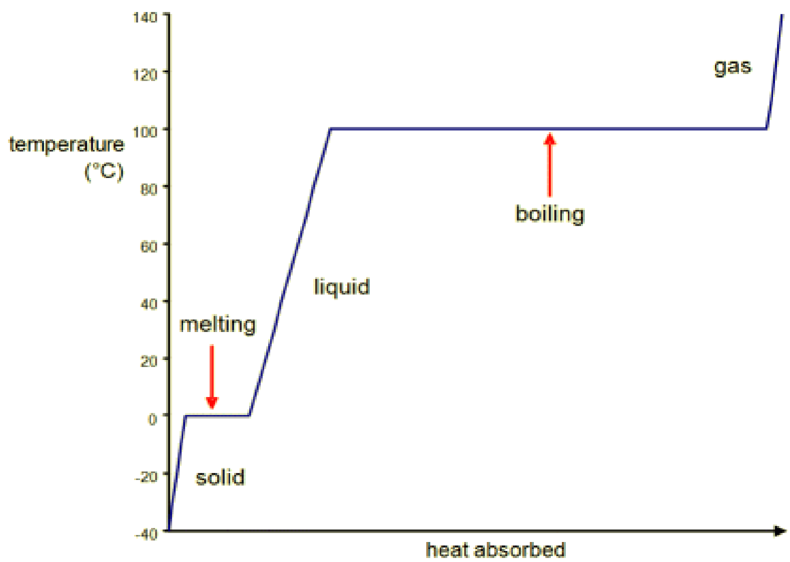
$(6^2 - \pi 3^2) = 1578\, m^2$. From melting down one ice hockey rink you can gain $1578 \cdot 2{,}5 \cdot 10^{-2} = 39{,}45\, m^3 = 39450\, l$ of water. Similar we can calculate the amount of water form melting down one ice hockey rink which corresponds to International hockey rules.
International hockey rink is bigger, so it contains **$4.1*10^4$** L of water. Source http://en.wikipedia.org/wiki/Ice_rink

2. If we assume that the density of water is $1000\, kg \cdot m^{-3}$, we have 39,45 $*10^3$ kg of water, therefore $39450 \cdot 333{,}55 \cdot 1000 = 1{,}316 \cdot 10^7\, kJ$ of heat is needed, it will cost $\left(\frac{1{,}316 \cdot 10^7}{3{,}6 \cdot 10^3}\right) \cdot 0{,}0743 = 272\, Ls$ (for NHL; not required to calculate)
286 Ls for international Ice hockey rink.

3. The reaction:

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

Actually, Le Chatelier's Principle with a change of pressure only applies to reactions involving volume changes. Increase of pressure leads to decrease of volume. During melting of ice volume decreases because density of water is smaller than density of ice. Volume changes are small, so pressure changes will have small effect on melting point. Increase of pressure leads to slight decrease of melting temperature.
4. The water has the largest value of heat of fusion; it can be explained by the fact that water forms STRONG hydrogen bonds unlike the other liquids.
5. The graph.



6. b (normal boiling point is at external pressure 1 atm; d – describes boiling at any conditions)
7. d
8. The reaction:

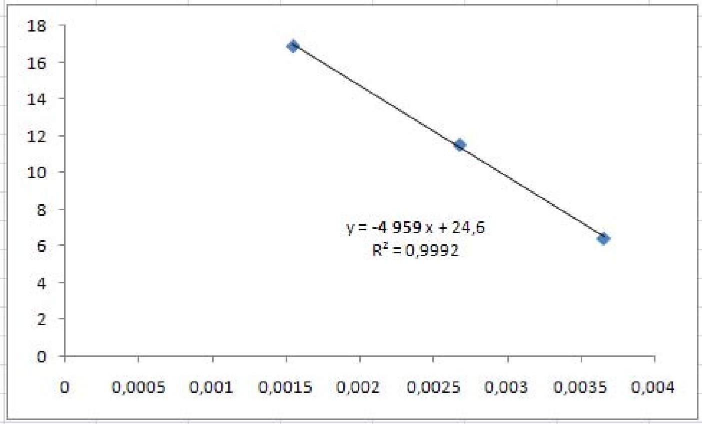
$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

The equilibrium of this reaction will move to the left if we increse the pressure. As pressure decreases water boils at more and more lower temperature (greater effect than in case of melting).
9. Equation $p = p_0 \cdot e^{-\frac{\Delta H}{RT}}$

$$\ln p = \ln p_0 - \frac{\Delta H}{RT}$$

Plotting ln p = f(1/T) you should obtain straight line with slope k = -ΔH/R.
It is the most precise method because it uses all three given data (not only two as in calculation by formula)

	A	B	C	D	E
1	0,6117	0,16			
2	101,325	100			
3	22060	373,946			
5	1/T	ln(p[kPa]*1000)			
6	0,003659	6,416242			
7	0,00268	11,52609			
8	0,001545	16,90928			
17			DH =	41229,13	J/mol
18				41,22913	kJ/mol



ΔH = 41.2 kJ/mol

Also use of Clapeiron equation 3 times and calculation of average value is accepted.

10. According to II Raoult's (*not Raul's, as mentioned in problem text*) rule and colligative properties, if we dissolve something (salts etc.) in solvent the temperature of freezing decreases. The rule shows how to calculate the freezing-point depression:

$$\Delta T = i \cdot c_M \cdot K_f,$$

Where i is isotonic coefficient, c_M – molality of dissolved compound, K_f – cryoscopic constant of solvent (water).

C_M can be calculated:

$$C_M = \frac{amount\ of\ \ compound\ (in\ moles)}{mass\ of\ \ solvent\ (kg)}$$

11. Calcium and magnesium sulphates completely dissociate in ions, i = 2.

$CaSO_4(s) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$

$MgSO_4(s) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$

We can assume density of solution equal to 1 g/mL and then mass of solvent is aprox. 1 kg.

$C_M = \frac{1.5 \cdot 10^{-3}}{1} = 1.5*10^{-3}$ mol/kg

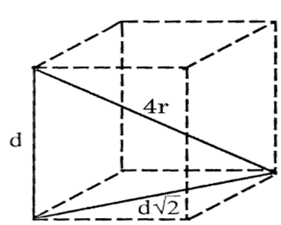
K_f(for water) = 1.86 K*kg/mol

$\Delta T = 2 \cdot 1.86 \cdot 1.5 \cdot 10^{-3} = 0.00558\ K \approx 0.006\,K$

12. We can easily reduce number of Ca^{2+} and Mg^{2+} ions by adding for example Na_3PO_4 to water:

$$3Ca^{2+} + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6Na^+$$
$$3Mg^{2+} + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 6Na^+$$
$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2$$
$$3Mg^{2+} + 2PO_4^{3-} \rightarrow Mg_3(PO_4)_2$$

13. As α-Fe has body-centered cubic unit cell and the lenght of the cell is given, we can calculate the atomic radius of iron in α-Fe.



$$d = 2.87 \text{ Å}$$
$$d\sqrt{3} = 4r$$
$$r = \frac{d\sqrt{3}}{4}$$
$$r = \frac{2.87 \cdot \sqrt{3}}{4} = 1.24 \text{ Å}$$

Let's now try to estimate Avogadro's number.

$$d = 2.87 \text{ Å} = 2.87 \ \cdot 10^{-8}\text{cm}$$

So the volume of the unit cell is:

$$d^3 = (2.87 \ \cdot 10^{-8})^3 = 2.36 \cdot 10^{-23} cm^3$$

There are d^{-3} unit cells in one *cm³* and as each bcc unit cell contains 2 atoms, we can calculate how many atoms are there in one *cm³*:

$$N = 2 \cdot d^{-3} = \frac{2}{2.36 \cdot 10^{-23}} = 8.47 \cdot 10^{22}$$

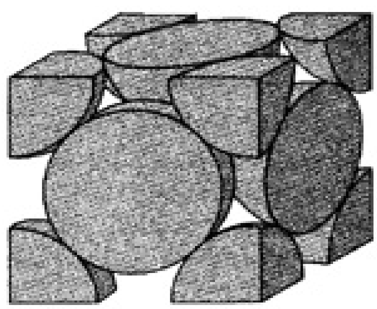
Avogadro's number is defined as the number of atoms or molecules in one mole. Iron has atomic mass 55.847 g/mol. The mass of $8.47 \cdot 10^{22}$ atoms (1 cm^3) is as given 7.86 g/cm^3, estimated Avogadro's number would be:

$$N_A = \frac{8.47 \cdot 10^{22} \cdot 55.847}{7.86} = 6.01 \cdot 10^{23} \ mol^{-1}$$

14. The edge lenght of fcc γ-Fe unit cell is:

$$d = 3.59 \text{ Å}$$

$d\sqrt{2} = 4r$ (see picture below)



$$r = \frac{d\sqrt{2}}{4}$$
$$r = \frac{3.59 \cdot \sqrt{2}}{4} = \mathbf{1.27} \text{ Å}$$

There are 4 Fe atoms in every unit cell, the unit cell has a volume of d^3:

$$d = 3.59 \text{ Å} = 3.59 \cdot 10^{-8} \ cm$$
$$d^3 = 4.63 \cdot 10^{-23} \ cm^3$$

The weight of unit cell:

$$m = \frac{4 \cdot M_{Fe}}{N_A}$$

$$m = \frac{4 \cdot 55.847}{6.0221 \cdot 10^{23}} = 3.7094 \cdot 10^{-22} \ g$$

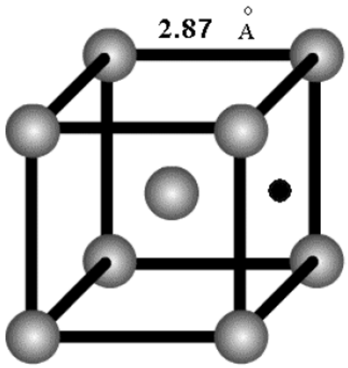
The density of γ-Fe:

$$\rho = \frac{m}{d^3}$$

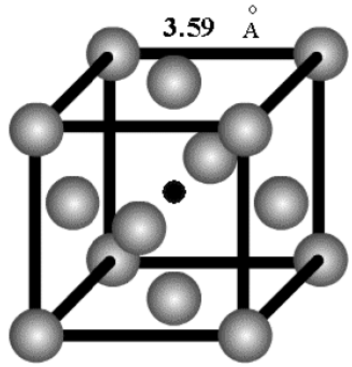
$$\rho = \frac{3.7094 \cdot 10^{-22}}{4.63 \cdot 10^{-23}} = \mathbf{8.01} \ \boldsymbol{g/cm^3}$$

15.

(c) and (d) The unit cells below are illustrated by using reduced size spheres. Note that, in hard spheres packing model <u>the represented atoms must be in contact one to each other</u>.



α-Fe



γ-Fe

According to the left figure, a perfectly fitted interstitial atom centered at (½, 0, ½) in an α-Fe cell, would have a radius of:

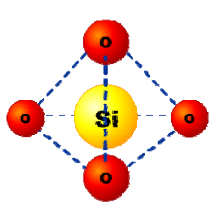
$R_{interstitial}$ = ½ a - R_{Fe}, where a = 2.87 Å and R_{Fe} = 1.24 Å [(see question (a)].
Therefore: $R_{interstitial}$ (α-Fe) ≈ 0.20 Å
Similarly, according to the figure in right, a perfectly fitted interstitial atom centered at (½, ½, ½) in an γ-Fe cell, would have a radius of:

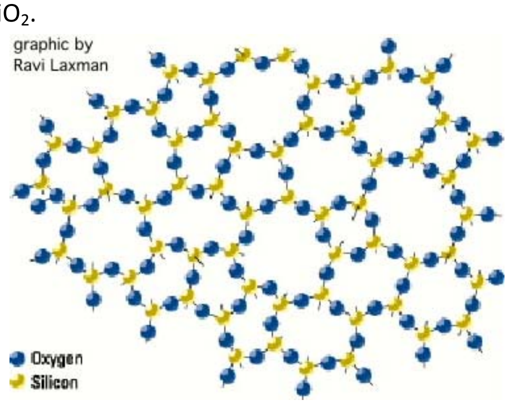
$R_{interstitial}$ = ½ a - R_{Fe}, where a =3.59 Å and R_{Fe}= 1.27 Å
Therefore: $R_{interstitial}$ (γ-Fe) ≈ 0.53 Å
(e) 1 nm = 10 Å. Thus:

For α-Fe: $$\frac{R_{carbon}}{R_{int\,erstitial}} = \frac{0.77\,\text{Å}}{0.20\,\text{Å}} = 3.85$$

For γ-Fe: $$\frac{R_{carbon}}{R_{int\,erstitial}} = \frac{0.77\,\text{Å}}{0.53\,\text{Å}} = 1.45$$

16. The most abundant chemical element in material **X** is oxygen, but main line in spectra corresponds to Si. By XRF method oxygen is almost impossible to determine.
17. The material **X** is **<u>fiberglass</u>** - silica (polymer $(SiO_2)_n$). Contains elements oxygen and silicon.
18. As the material does not have exact melting point it is amorphous.
19. The compound **Y** is SiO_2.





Coordination number for silicon is 4, for oxygen 2.

20. Silicon is commercially prepared by the reaction of high-purity silica with wood, charcoal, and coal, in an electric arc furnace using carbon electrodes. At temperatures over 1900 °C, the carbon reduces the silica to silicon according to the chemical equations:

$SiO_2 + C \rightarrow Si + CO_2$

$SiO_2 + 2\ C \rightarrow Si + 2\ CO$

Liquid silicon collects in the bottom of the furnace, and is then drained and cooled. The silicon produced via this process is called *metallurgical grade silicon* and is at least 98% pure. Using this method, silicon carbide (SiC) may form. However, provided the concentration of SiO_2 is kept high, the silicon carbide can be eliminated:

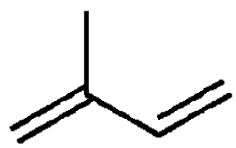
$2\ SiC + SiO_2 \rightarrow 3\ Si + 2\ CO$ [source http://en.wikipedia.org/wiki/Silicon]

There are no practical applications of oxygen production from SiO_2, but theoretically it can be done:

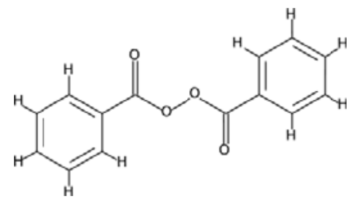
$SiO_2 + Mg \rightarrow 2MgO + Si$ and then electrolysis: $MgO(l) \rightarrow Mg(s) + ½O_2(g)$

Other methods are also possible.

21. Structures:

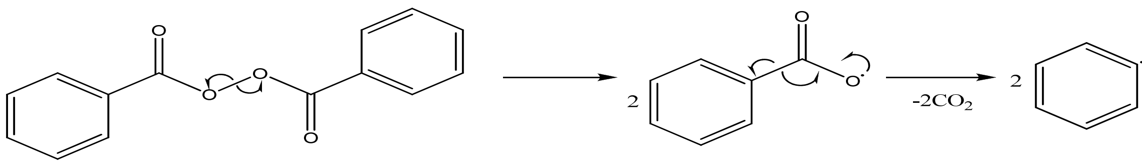


isoprene

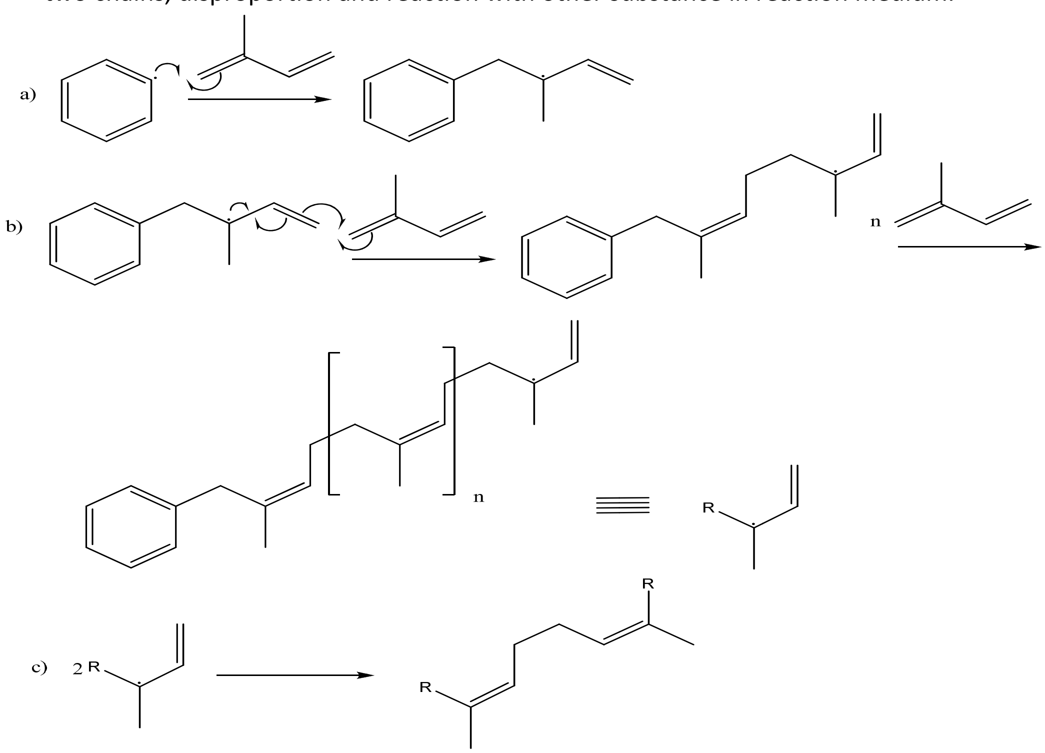


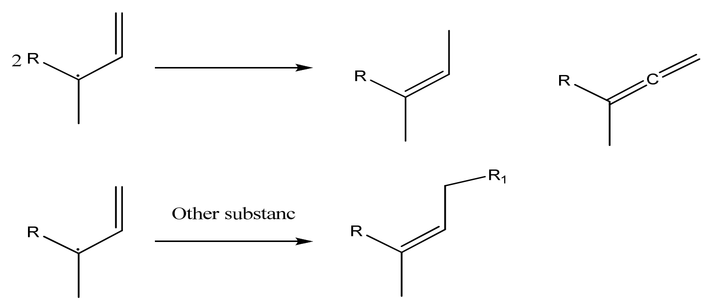
benzoyl peroxide

22. Benzoyl peroxide generates free radicals, which initiates the polymerization.



23. In the scheme there are showed a) chain initiation, b) chain growth and c) chain termination by combination of two chains, disproportion and reaction with other substance in reaction medium.





24. If the weight of hockey puck is 160 g, sulphur content is 10% and the yield of the reaction is 86% then there is necessary 160·0,90/0,86 = **<u>167,4 g</u>** of isoprene.

25. Mass of isoprene is 160·0,90 = 144 g.

Amount of isoprene is n = m/M = 144/68,12 = 2,114 mol

Amount of isoprene molecules is $N = n \cdot N_A = 2{,}114 \cdot 6{,}022 \cdot 10^{23} = 1{,}273 \cdot 10^{24}$

Amount of isoprene molecules in one macromelocule: X = M(macromol)/M(isopr) = 250000/68,12 = 3670 molecules

Amount of macromolecules in puck is : N(macromol) = N/X = $1{,}273 \cdot 10^{24}$/3670 = $\mathbf{3{,}469 \cdot 10^{20}}$

Amount of sulphur in puck is: m·w/M = 160·0,10/32,06 = 0,499 mol

Amount of sulphur atoms is: $N(S) = n \cdot N_A = 0{,}499 \cdot 6{,}022 \cdot 10^{23} = 3{,}005 \cdot 10^{23}$

Sulphur atoms per one macromolecule = N(S)/ N(macromol) = $3{,}005 \cdot 10^{23} / 3{,}469 \cdot 10^{20}$ = **866**

If sulphur – sulphur bond is assumed as consisting of two atoms and if there are counted double number of the bonds (because sulphur atoms what is bonded to closest molecules also bonds with examined molecule), then the number of bonds is **866**, but if bond is assumed as consisting of three sulphur atoms, there are **577** bonds.

Monomers per one sulphur atom = 3670/866 = **4,24**

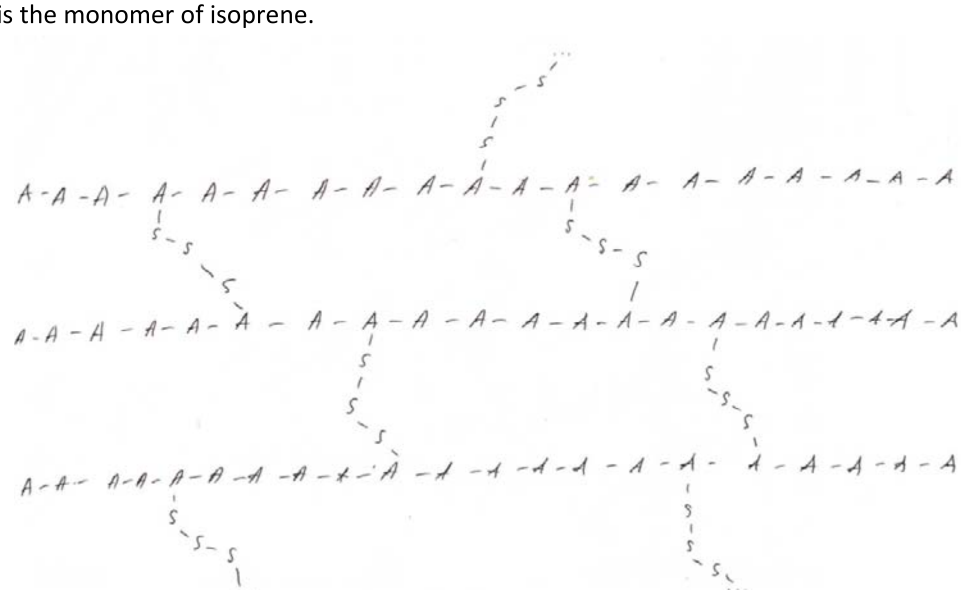
26. For this the volume of the puck has to be calculated:

$V = \pi \cdot R^2 \cdot H = \pi \cdot (0{,}038\text{m})^2 \cdot 0{,}025\text{m} = 1{,}134 \cdot 10^{-4}\ \text{m}^3$

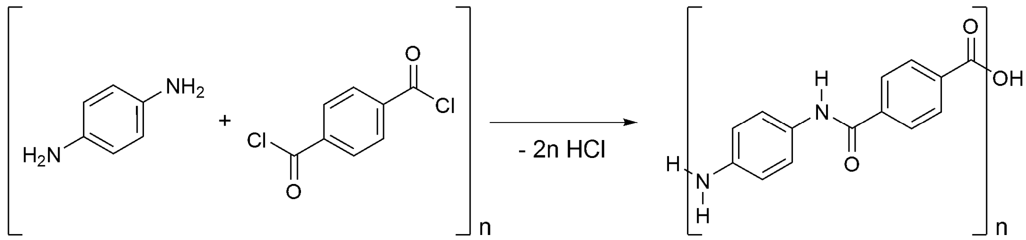
V(macromol) = V/N(macromol) = $1{,}134 \cdot 10^{-4} / 3{,}469 \cdot 10^{20} = 3{,}269 \cdot 10^{-25}\ \text{m}^3 = 327\ \text{nm}^3$

In this way volume of the macromolecule with 866 related sulphur atoms are calculated.

27. If there are 4,24 monomers per sulphur atom then if the bond consists of thee sulphur atoms there are 12,75 ≈ 13 monomers per one bond what forms from given molecule, so the sulphur binding can look like in picture, where A is the monomer of isoprene.

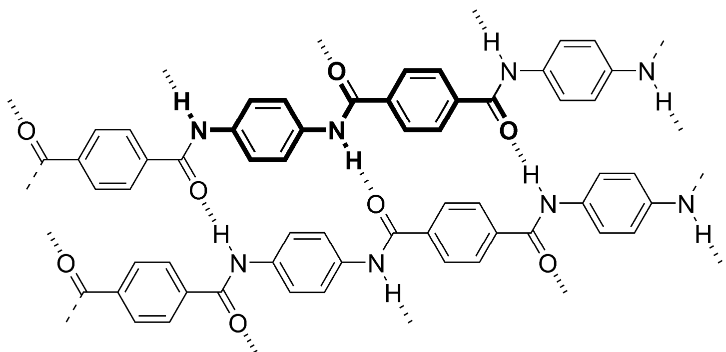


28. Material **Q** is kevlar while compound **W** is hydrogen chloride / hydrochloric acid.



29. Hydrogen bonds

Additional strength is derived from aromatic stacking interactions between adjacent strands. These interactions have a greater influence on Kevlar than the van der Waals interactions and chain length that typically influence the properties of other synthetic polymers; structure:



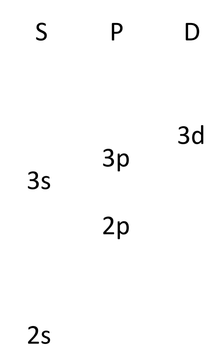
30. Kevlar (poly paraphenylene terephthalamide) production is expensive because of the difficulties arising from using concentrated sulfuric acid, needed to keep the water-insoluble polymer in solution during its synthesis and spinning. Second reason for use of sulfuric acid is that it associates with water which also forms in condensation reaction.

Correct answer to each question was awarded with 0.5 points, except questions 6. and 7. They gave 0.25 points each.

Problem 3 (Estonia)
Everyone loves spectra (10 points)
Corrected problem

Colour of a firework or a flame in a flame test is an evidence of photon emission at frequency range 430–750 THz. Let's find out how emission happens in alkaline elements atoms.

When the electrons in the atom are excited (by heating for example), they jump to higher energy levels. As the electrons fall back down, energy is re-emitted, the wavelength of which refers to the discrete lines of the emission spectrum. The photon energy due to an electron transition between an exited atomic level k (of energy E_k) and a lower level i is $\Delta E = E_k - E_i = h\nu = hc/\lambda$, where ν is the frequency, and λ the wavelength. Since a photon carries energy and angular momentum (1 unit), any electronic transition from one allowed energy level to another must conserve energy and angular momentum for the atom-photon system. These restrictions are known as selection rules and they are, $\Delta S = 0$, $\Delta L = \pm1$, and $\Delta J = 0, \pm1$, with $J = 0$ to $J = 0$ forbidden. Allowed transition between electronic states in alkaline elements atoms obeys these selection rules.



Energy level diagram

1. *Schematic presentation of energy levels – energy level diagram, is shown. Mark allowed transitions by arrows which lead to 2s and 2p configurations.*

All the allowed transitions may be easily calculated, if electronic configuration energies are known. Persistent lines in the visible spectrum of alkaline elements mainly due prior to transitions between *n*p[1], (*n* + 1)p[1] , and *n*s[1] configuration. The energy of corresponding levels of an upper electron may be obtained by: $E = -13.6 \cdot Z_{\text{eff}}^2 / n^2$, where Z_{eff} is the effective nuclear charge ($Z_{\text{eff}} < Z$), and *n* is the principal quantum number. Value of Li ionization energy (5.3917 eV) may be used to estimate Z_{eff}(2s). Z_{eff} value for an electron on 2p and 3p levels in Li atom is 0.25 and 0.75 units lower than Z_{eff}(2s), respectively. Z_{eff}(*n*s) in other alkaline elements atoms increased by 0.485 in the transition to the next period. Similarly Z_{eff} (*n*p) and Z_{eff} ((*n* + 1)p) increased by 0.389 and 0.114.[1]

2. *Calculate photon wavelength due to an electron transition between np or (n + 1)p and ns levels of alkaline elements from Li to Cs.*

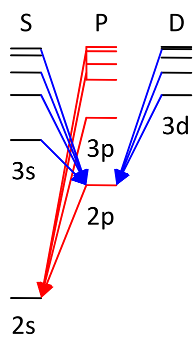
Calculated values may be now used to predict the colours of the alkali compounds in firework or flame. Assume, that calculated values are differ from experimental data by ±100 nm in average except for lithium.

3. *In visible spectra of Li is another persistent line (610 nm). Which transition does it belong to?*
4. *Compounds of which alkali elements give colour to yellow, red and violet firework?*

More information about this problem: *http://eko.olunet.org/2010/01/15/lost-in-translation/*

Solution

a)



Energy level diagram

b) $IE = E' - E = -13.6 \cdot \left(\frac{2Z_{\text{eff, 1s}}^2}{1^2} \right) + 13.6 \cdot \left(\frac{2Z_{\text{eff, 1s}}^2}{1^2} + \frac{Z_{\text{eff, 2s}}^2}{2^2} \right) = 13.6 \cdot \frac{Z_{\text{eff, 2s}}^2}{2^2} = 5.3917 \text{ eV}$

Li: $Z_{\text{eff, 2s}} = 2 \cdot \sqrt{\frac{5.3917}{13.6}} = 1.259$

Li: $Z_{\text{eff, 2p}} = 1.259 - 0.25 = 1.009$

[1] These simplified data were adjusted based on photon wavelength values from the experimental spectra.

$$\lambda = 6.626\cdot 10^{-34}\cdot 3.00\cdot 10^{8}\Big/ 1.602\cdot 10^{-19}\cdot 13.6\left(\frac{Z_{\text{eff, 2s}}^2}{2^2}-\frac{Z_{\text{eff, 2p}}^2}{2^2}\right)=$$

$$= 91.2\text{ nm}\Big/\left(\frac{1.259^2}{2^2}-\frac{1.009^2}{2^2}\right) = 643\text{ nm}$$

Li: $Z_{\text{eff, 3p}} = 1.259 - 0.75 = 0.509$ λ = 248 nm

Na: $Z_{\text{eff, 3s}} = 1.259 + 0.485 = 1.744$

Na: $Z_{\text{eff, 3p}} = 1.009 + 0.389 = 1.398$ λ = 755 nm

Na: $Z_{\text{eff, 4p}} = 0.509 + 0.114 = 0.623$ λ = 291 nm

K: $Z_{\text{eff, 4s}} = 1.744 + 0.485 = 2.229$

K: $Z_{\text{eff, 4p}} = 1.398 + 0.389 = 1.787$ λ = 822 nm

K: $Z_{\text{eff, 5p}} = 0.623 + 0.114 = 0.737$ λ = 316 nm

Rb: $Z_{\text{eff, 5s}} = 2.229 + 0.485 = 2.714$

Rb: $Z_{\text{eff, 5p}} = 1.787 + 0.389 = 2.176$ λ = 867 nm

Rb: $Z_{\text{eff, 6p}} = 0.737 + 0.114 = 0.851$ λ = 332 nm

Cs: $Z_{\text{eff, 6s}} = 2.714 + 0.485 = 3.199$

Cs: $Z_{\text{eff, 6p}} = 2.176 + 0.389 = 2.565$ λ = 898 nm

Cs: $Z_{\text{eff, 7p}} = 0.851 + 0.114 = 0.965$ λ = 344 nm

c) 3d→2p

d) Li has also orange and red lines. Li_2CO_3 is used for colouring fireworks in red. (*n*+1)s→*n*p transition appear in violet–blue part of visible spectrum starting from K. KNO_3 and $RbNO_3$ are used for colouring fireworks in violet and violet-red. *n*p→*n*s transition is shifted to red (K, 722 nm) down the group, thus we may guess, that Na should give yellow colouring, (<655 nm). $NaNO_3$ is used in fireworks.