Baltic Chemistry Competition

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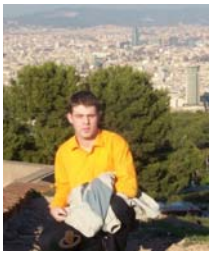
2ND ROUND, PROBLEMS

Solve all or some of the four problems given on the next pages and write your answers in *MS Excel* answer sheets provided. If there are some explanations required, write them in English or Russian. Please, send your answers to: kimijas_olimpiades@inbox.lv **till 28.12.2009. at 24:00**. Answers which will be sent after this time will not be graded. Write all the answers in one workbook but in different worksheets for each problem. You should fill in the green spaces provided.

File name must consist from your name, surname (in English) and country, for example *John_Black_England.xls* (or *.xlsx). If you do not name the file as described you will receive 3 point penalty. For all correctly solved problems you can get the maximum of 30 points. The exact amount of points for each task is given at the top of each problem.

All students who will be taking part in at least one round will participate in the final round which will be held on the web on 27th of February. During the final round you will have to solve the multiple choice test.

Authors for problems in this round:



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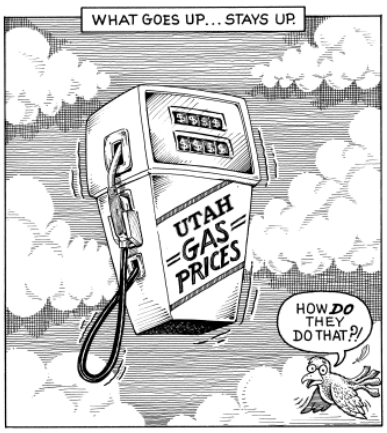
Good luck with problem solving! ☺

If you have any questions, address them to us in English and send them to: kimijas_olimpiades@inbox.lv
Feel free to ask!



Problem 1 (Latvia*)

Unknown highly flammable gas (6 points)

Compound **A** is a colorless highly flammable gas containing 21.7% of Hydrogen by mass (use atomic masses with one decimal place). It undergoes pyrolysis at temperatures above 100°C. The process is very complicated, but the first steps can be described by the following equations:

$$A \xrightarrow{\text{fast}} 2\{B\}$$

$$A + \{B\} \xrightarrow{\text{fast}} \{C\}$$

$$\{C\} \xrightarrow{\text{rate determining step}} D + H_2$$

$$\{B\} + \{D\} \rightarrow E$$

$$A + \{D\} \rightarrow \{B\} + E \rightarrow F + H_2$$

Compounds in brackets {} are unstable intermediates.

1) *What is compound **A**? Draw its structure and describe the bonding in its molecule.*
2) *Determine the formulae of compounds **B – F**.*
3) *At room temperature **B** dimerises into **A**. Why does not **B** exist in monomer form?*

** There will be two Lithuanian problems in next round.*

Problem 2 (Latvia)

Chemistry of Ice hockey (14 points)

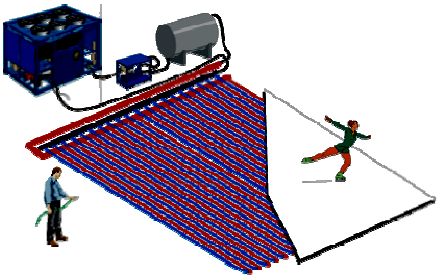
Martin Prusek (Czech goalkeeper) and Sandis Ozoliņš (#8, only Latvian who has won Stanley cup) in forms of Dinamo Riga, 2009-2010 KHL season

The ice hockey definitely is most popular sport in Latvia, only then come basketball, soccer and others. The highest point of fan activity is in each year's May, because then Latvian national ice hockey team participates in World championship, division A.

Starting from 2008 year Riga has hockey team Dinamo Riga which participates in Continental Hockey League (KHL) championship so fans can enjoy hockey game almost all year. Home games of Dinamo Riga are played in Arena Riga which lies only half mile form Department of Chemistry, University on Latvia.

Let's take a look to things which we need if we want to play ice hockey.

The first thing we need is **ice**. In modern rinks ice are produced by pipes spraying thin layer of cold water on concrete (pictured). Then this thin layer is painted white (for better contrast) and all necessary markings and logos are painted on it. Then another layer of cold water is sprayed on it. Thickness of ice is approximately 2-3 cm.



1. *Let's assume that ice thickness in arena is 2.5 cm. Calculate how many liters of water you can gain if you melt down one ice hockey rink which corresponds to International hockey rules and one ice hockey rink which corresponds to NHL rules! Use any appropriate information source for searching for size of rinks and other info.*
2. *Water enthalpy of fusion is 333.55 J/g. Calculate how much heat is required to melt down international ice hockey arena. If price for electricity in Latvia is 0.0743 Ls per kW·h, then how much it will cost?*
3. *How does change in pressure affects melting of ice? Explain your answer using Le Chatellier principe. Please write your explanations in English.*
4. *Compare heat of fusion for water with heats of fusion for other liquids such as benzene, pentane, acetone and ethanol, explain differences according to bonding. Please write your explanations in English.*
5. *When heat is added to water it can be evaporated. Sketch the graph showing temperature change against heat added.*
6. *The normal boiling point of water is: (chose one the most correct answer)*
   a. *100.00^{o}C at any conditions*
   b. *is the temperature at which the vapor pressure is 1 atm*
   c. *is the temperature at which liquid and vapor are in equilibrium*
   d. *is the temperature at which the vapor pressure equals the external pressure*
   e. *is the temperature at which there is a continuous formation of gaseous bubbles in liquid.*
7. *The vapor pressure of given liquid will increase if: (chose one the most correct answer)*
   a. *the liquid is moved to a contained in which its surface is very much larger*
   b. *the volume of liquid is increased*
   c. *the volume of vapor phase is increased*
   d. *temperature is increased*
   e. *a more volatile liquid is added to the given liquid.*
8. *How does change in pressure affects boiling of water? Explain your answer using Le Chatelier's principle. Please write your explanations in English.*

9. *Change of pressure over temperature can be calculated by equation $p = p_0 \cdot e^{-\frac{\Delta H}{RT}}$, where p – pressure; p_0 – constant, R = 8.314 J/(mol·K), ΔH – enthalpy of vaporization, T – temperature (in K). Use any method to determine p_0 and ΔH as precise as you can if such thermodynamical data are given:*

	Pressure, kPa	*Temperature, °C*
Triple point of water	*0.6117*	*0.160*
Normal boiling point	*101.325*	*100*
Critical point	*22060*	*373.946*

Show your calculations!

After 1st and 2nd period of hockey game ice washed and cleaned for next part of games. Washing process removes any foreign material that might otherwise become embedded in the ice surface. At the rear of the conditioner, a sprinkler pipe wets a cloth towel that lays down clean water to fill the residual grooves, and forms a new ice surface. Hot water (60°C) is frequently used where available because it melts and smoothes the rough top layer of ice to create a flat, smooth surface. This water in many rinks is filtered and treated before being heated to remove any residual minerals and chemicals in the water. These chemicals and minerals could otherwise make the ice brittle or soft, give it pungent odors, or make it cloudy.

10. *How do chemicals and minerals dissolved in water affect temperature of freezing? Use Raul's rules to explain this. Please write your explanations in English.*
11. *Calculate temperature of freezing for tap water which contains sum of calcium sulfate and magnesium sulfate equal to 1.5 mmol per L.*
12. *Write molecular and net ionic equation which can show how to reduce number of Ca^{2+} and Mg^{2+} in water!*

The second thing you need is **skates**. It is made out of carbon steel rather than stainless steel. Goalie skates differ from regular hockey skates. The blade is longer, wider, and flatter to provide the goalie with more stability. The blade is shorter vertically so that the goaltender is lower to the ice.

Iron can exist in more crystalline forms. The crystalline form of iron, known as α-Fe, has a *body centered cubic* (bcc) unit cell with an edge length of 2.87 Å. Its density at 25 °C is 7.86 g/cm^3. Another – higher temperature - crystalline form, known as γ-Fe, has a *face centered cubic* (fcc) unit cell with an edge length of 3.59 Å.

13. *Calculate the atomic radius of iron in α-Fe and use the above facts to estimate Avogadro's number.*
14. *Calculate the atomic radius of iron in γ-Fe as well as the density of γ-Fe.*
15. *Calculate radius of largest atom which can be inserted in holes of α-Fe and γ-Fe. How much oversize in both cases is a carbon atom, having a radius of 0.077 nm?*

Next thing we have to use for hockey game is stick. Traditional sticks were usually made completely of wood, most modern sticks are reinforced with graphite and material X (pictured) and the paddle and blade are injected with foam to make them lighter.

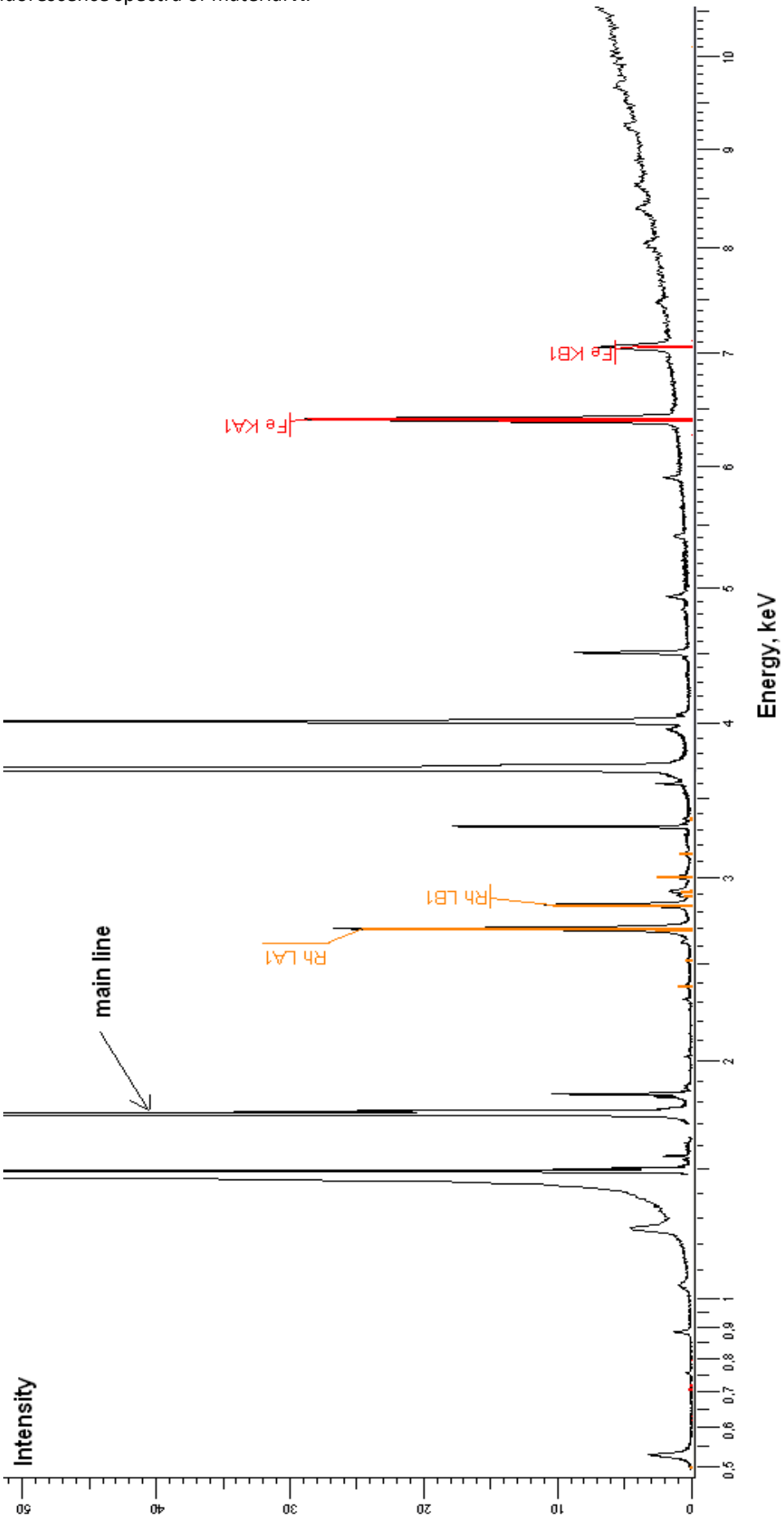
X-ray fluorescence spectra for material **X** is given in next page. Knowing that each spectral lines can be calculated by equation E = a * z + b, where E – energy of spectral line, keV; z – position in spectra from edge of paper, cm; a and b – empirical constants. Using given spectra and table of spectral lines for heavy elements answer questions 16.-17. A spectrum is obtained by x-ray fluorescence spectrometer S8 Tiger Bruker, University of Latvia, Department of Chemistry.

Table of spectral line energies

		M - серия	L - серия									K - серия				
					Lα1,2								Kα1,2		Kβ1,3	
No.	Символ	Mα	Ll	Lα2	Lα1	Ln	Lβ4	Lβ1	Lβ2	Lβ3	Lγ1	Kα2	Kα1	Kβ3	Kβ1	Kβ2
6	C												0.2777			
7	N												0.392			
8	O												0.525			
9	F												0.677			
10	Ne												0.848			
11	Na												1.041			
12	Mg												1.253			
13	Al												1.486		1.553	
14	Si												1.739		1.829	
15	P												2.013		2.136	
16	S												2.307		2.464	
17	Cl												2.621		2.815	
18	Ar												2.957		3.19	
19	K												3.312		3.589	
20	Ca				0.341								3.69		4.012	
21	Sc				0.395								4.088		4.46	
22	Ti				0.452								4.508		4.931	
23	V				0.511								4.949		5.426	
24	Cr				0.537			0.583					5.411		5.946	
25	Mn				0.637			0.649					5.894		6.489	
26	Fe				0.705			0.718					6.398		7.057	
27	Co				0.776			0.791					6.924		7.648	
28	Ni				0.851			0.869					7.471		8.263	
29	Cu				0.903			0.95					8.04		8.904	
30	Zn				1.012			1.034					8.63		9.57	
31	Ga				1.098			1.125					9.241		10.262	
32	Ge				1.188			1.218					9.874		10.979	
33	As				1.282			1.317					10.53		11.722	
34	Se				1.379			1.419					11.207		12.492	
35	Br				1.48			1.526					11.907		13.287	
36	Kr				1.586			1.636					12.631		14.108	
37	Rb				1.694			1.752					13.373		14.966	15.202
38	Sr				1.806			1.871					14.14		15.831	16.082
39	Y				1.922			1.995					14.931		16.733	17.013
40	Zr				2.042			2.124				15.688	15.772		17.66	17.967
41	Nb				2.166			2.257	2.367		2.461	16.518	16.612		18.61	18.949
42	Mo				2.293			2.394	2.518		2.623	17.371	17.476		19.6	19.962
43	Tc				2.424			2.536				18.248	18.364		20.608	21.002
44	Ru				2.558			2.683	2.835		2.964	19.147	19.276	21.631	21.653	22.07
45	Rh		2.376		2.696	2.519		2.834	3.001		3.143	20.07	20.213	22.695	22.72	23.169
46	Pd		2.503		2.838	2.66		2.99	3.171		3.328	21.017	21.174	23.787	23.815	24.295
47	Ag		2.633		2.984	2.806		3.15	3.347		3.519	21.987	22.159	24.907	24.938	25.452
48	Cd		2.767		3.133	2.956		3.316	3.528		3.716	22.98	23.17	26.057	26.091	26.639
49	In		2.904		3.286	3.112		3.487	3.713		3.92	23.998	24.206	27.233	27.271	27.856
50	Sn		3.044		3.443	3.272		3.662	3.904		4.13	25.04	25.267	28.439	28.481	29.104
51	Sb		3.188		3.604	3.436		3.843	4.1		4.347	26.106	26.355	29.674	29.721	30.388

		M - серия	L - серия									K - серия				
					Lα1,2								Kα1,2		Kβ1,3	
No.	Символ	Mα	Ll	Lα2	Lα1	Ln	Lβ4	Lβ1	Lβ2	Lβ3	Lγ1	Kα2	Kα1	Kβ3	Kβ1	Kβ2
52	Te		3.335		3.769	3.607		4.029	4.301		4.57	27.197	27.468	30.939	30.99	31.698
53	I		3.484		3.937	3.78		4.22	4.507		4.8	28.312	28.607	32.234	32.289	33.036
54	Xe				4.109			4.422	4.72		5.036	29.453	27.774	33.556	33.619	34.408
55	Cs		3.794		4.286	4.141		4.686	4.935		5.279	30.62	30.968	34.913	34.981	35.815
56	Ba		3.953		4.465	4.33		4.839	5.156		5.53	31.812	32.188	36.298	36.372	37.251
57	La	0.833	4.124		4.65	4.524		5.053	5.383		5.788	33.028	33.436	37.714	37.795	38.723
58	Ce	0.883	4.287		4.839	4.731		5.272	5.612		6.051	34.273	34.714	39.163	39.251	40.226
59	Pr	0.929	4.452		5.033	4.935		5.401	5.849		6.321	35.544	36.02	40.646	40.741	41.767
60	Nd	0.978	4.632		5.229	5.145		5.732	6.088		6.601	36.841	37.355	42.159	42.264	43.327
61	Pm	1.03			5.432			5.922	6.338		6.891	38.165	38.718	43.705	43.818	44.929
62	Sm	1.081	4.994		5.635			6.214	6.586		7.177	39.516	40.111	45.281	45.405	46.566
63	Eu	1.131	5.176		5.845			6.465	6.842		7.479	40.895	41.535	46.896	47.03	48.248
64	Gd	1.185	5.361		6.056			6.72	7.102		7.784	42.302	42.989	48.547	48.688	49.952
65	Tb	1.24	5.546		6.272	6.283		6.985	7.365		8.1	43.737	44.474	50.221	50.374	51.715
66	Dy	1.293	5.742		6.494	6.533		7.255	7.634		8.417	45.2	45.991	51.949	52.11	53.5
67	Ho	1.347	5.942		6.719	6.787		7.532	7.91		8.746	46.692	47.539	53.702	53.868	55.315
68	Er	1.405	6.152		6.947	7.057		7.823	8.188		9.087	48.213	49.119	55.485	55.672	57.204
69	Tm	1.462	6.341		7.179	7.308		8.1	8.467		9.424	49.764	50.733	57.293	57.506	59.085
70	Yb	1.521	6.544		7.414	7.579		8.4	8.757		9.778					
71	Lu	1.581	6.752		7.654	7.856		8.708	9.038		10.142					
72	Hf	1.644	6.958	7.843	7.898	8.138	8.904	9.021	9.346	9.162	10.514					
73	Ta	1.709	7.172	8.086	8.145	8.427	9.211	9.342	9.65	9.486	10.893					
74	W	1.774	7.386	8.334	8.396	8.723	9.524	9.671	9.96	9.817	11.284					
75	Re	1.842	7.602	8.585	8.651	9.026	9.845	10.008	10.274	10.158	11.683					
76	Os	1.914	7.821	8.84	8.91	9.335	10.174	10.354	10.597	10.509	12.093					
77	Ir	1.98	8.04	9.098	9.174	9.649	10.509	10.706	10.919	10.866	12.51					
78	Pt	2.048	8.267	9.36	9.441	9.973	10.852	11.069	11.249	11.233	12.94					
79	Au	2.123	8.493	9.626	9.712	10.307	11.203	11.44	11.583	11.608	13.379					
80	Hg	2.195	8.72	9.896	9.987	10.649	11.561	11.821	11.922	11.993	13.828					
81	Tl	2.267	8.952	10.171	10.267	10.992	11.929	12.211	12.27	12.388	14.289					
82	Pb	2.342	9.183	10.448	10.55	11.347	12.304	12.612	12.621	12.791	14.762					
83	Bi	2.419	9.419	10.729	10.837	11.71	12.689	13.021	12.978	13.208	15.245					
84	Po	2.5	9.662	11.014	11.129		13.083	13.445	13.338	13.635	15.741					
85	At	2.6		11.303	11.425			13.874	14.065		16.249					
86	Rn	2.7		11.596	11.725			14.313	14.509		16.768					
87	Fr	2.78		11.893	12.029			14.768	14.448	14.973	17.3					
88	Ra	2.86	10.62	12.194	12.338	13.661	14.745	15.233	14.839	15.442	17.845					
89	Ac	2.93		12.499	12.65			15.71	15.227	15.929	18.405					
90	Th	2.996	11.117	12.807	12.967	14.507	15.64	16.199	15.621	16.423	18.979					
91	Pa	3.082	11.364	13.12	13.288	14.944	16.101	16.699	16.022	16.929	19.565					
92	U	3.164	11.616	13.437	13.612	15.397	16.573	17.217	16.425	17.452	20.164					
93	Np	3.29	11.887	13.757	13.942	15.874	17.058	17.747	16.837	17.986	20.781					
94	Pu	3.38	12.122	14.082	14.276	16.33	17.553	18.291	17.252	18.537	21.414					
95	Am	3.47	12.381	14.409	14.615		18.06	18.849	17.673	19.103	22.061					
96	Cm			14.74	14.953			19.399	18.096		22.703					
97	Bk			15.08	15.304			19.961	18.529		23.389					

X-ray fluorescence spectra of material **X**:



16. *Which is the most abundant chemical element in material **X**?*

17. *Determine the qualitative composition of material **X**. What is material **X** (in English)?*

18. *A material **X** has no exact melting point. What does it mean about solid state structure of **X**? Explain. Please write your explanations in English.*

19. *The most abundant element in material **X** is widely spread in nature. Write formula for compound **Y** containing this element which is the most abundant form of mentioned element in nature. Draw structure for this compound in solid state and determine coordination numbers for all elements in this compound.*

20. *Write equations for reactions which show how to obtain pure elements starting from compound **Y**.*

The fourth thing in hockey play we need is the **puck**. Hockey puck is made from vulcanized rubber and its parameters are: 25 mm thick, 76 mm in diameter and it weights 160 g. Normally rubber is made synthetically from isoprene by free radical polymerization with 86 % yield. In synthesis benzoyl peroxide is added to mixture. In synthesis polyisoprene forms with molecular weight 100 000 – 1 000 000 g/mol (in your calculations assume that it is 250 000 g/mol). It was determined, that hockey puck contains 10 % of sulfur.

21. *Write down structures of isoprene and benzoyl peroxide.*
22. *What role in synthesis benzoyl peroxide has? Write down reaction mechanism for its conversation.*
23. *Write down mechanism of synthesis of polyisoprene in these conditions by showing precisely all steps: a) chain initiation, b) chain growth and c) chain termination.*
24. *By assuming all given information, calculate how much isoprene is necessary for this reaction.*
25. *By assuming all given information, calculate how many macromolecules form one hockey puck. How many sulfur atoms has per one macromolecule? How many sulfur-sulfur bonds form one macromolecule? Calculate how many monomers there are per one sulfur atom?*
26. *By assuming all given information, calculate the volume of one macromolecule. Volume for what actually is calculated in this way?*
27. *Show the sulfur binding in this hockey puck for three bonded macromolecules.*

The fifth and today the last thing we need is **masks** (introduced only in 1959 by Canadian goalkeeper Jacques Plante, Montreal Canadiens, NHL). Nowadays there are no players to play without mask (it is prohibited). 1st type of masks was only in from of face, 2nd type is helmet-cage type mask nowadays used only by some goalkeepers (among them Martin Prusek from Dinamo Riga, pictured at the beginning) and 3rd type of mask with a cage attached in the middle is used by most of goalies (pictured Edgars Masaļskis representing Dinamo Riga, Latvian National team). The last type of masks is thought to be safer. It is made from fiberglass and material **Q**.

This material is synthesized in solution from the monomers *para*-phenylenediamine and terephthaloyl chloride in a condensation reaction yielding compound **W** as a byproduct.

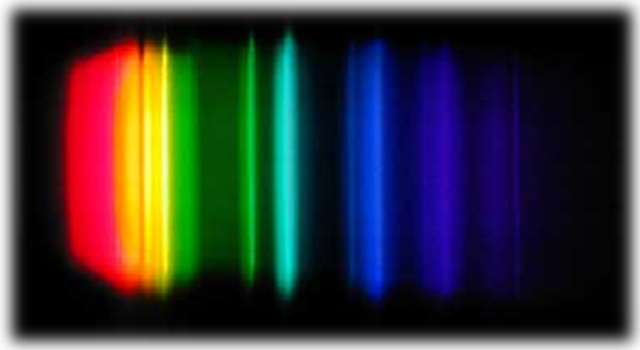
28. *Write equation for synthesis of material **Q**. What is the name of it? What is compound **W**?*

29. *What makes material **Q** so strong? Explain it from point of chemistry by drawing corresponding structure.*

30. *Concentrated sulfuric acid is used for synthesis of compound **Q**. Explain why sulfuric acid is necessary for this synthesis (take in account at least two reasons)? Please write your explanation in English.*

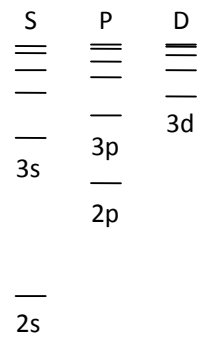
Problem 3 (Estonia)

Everyone loves spectra



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, $\Delta S = 0$, $\Delta L = \pm 1$, and $\Delta J = 0, \pm 1$, 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 from np^1 or $(n + 1)p^1$ to the ns^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}. Value of Li ionization energy (5.3917 eV) may be used to estimate $Z_{\text{eff}}(2s)$. Z_{eff} of electron on 2p and 3p levels in Li atom is 0.25 and 0.75 bigger than $Z_{\text{eff}}(2s)$ respectively. $Z_{\text{eff}}(ns)$ in other alkaline elements atoms increased by 0.485 in the transition to the next period. Similarly Z_{eff} (np) and Z_{eff} ((n + 1)p) increased by 0.389 and 0.114.[1]

2. *Calculate photon wavelength due to an electron transition between* n*p or (*n *+ 1)p and* n*s 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 overestimated; they are higher, than experimental data by 100 nm in average.

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?*

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