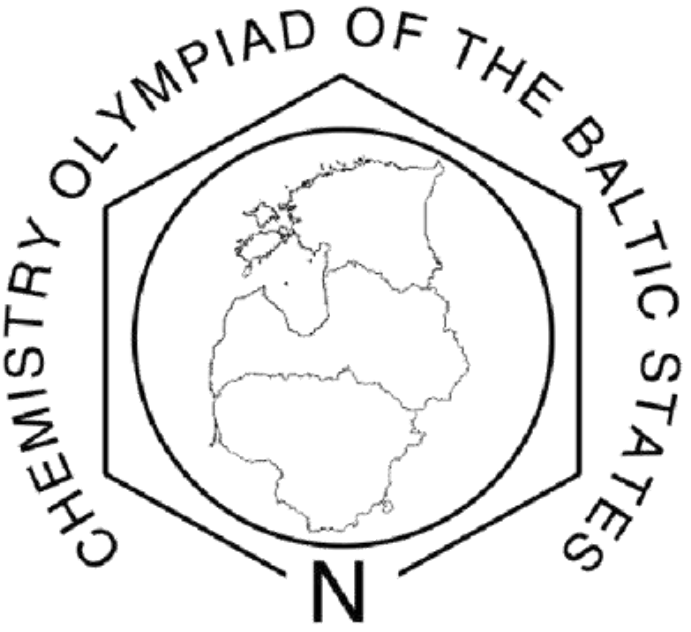
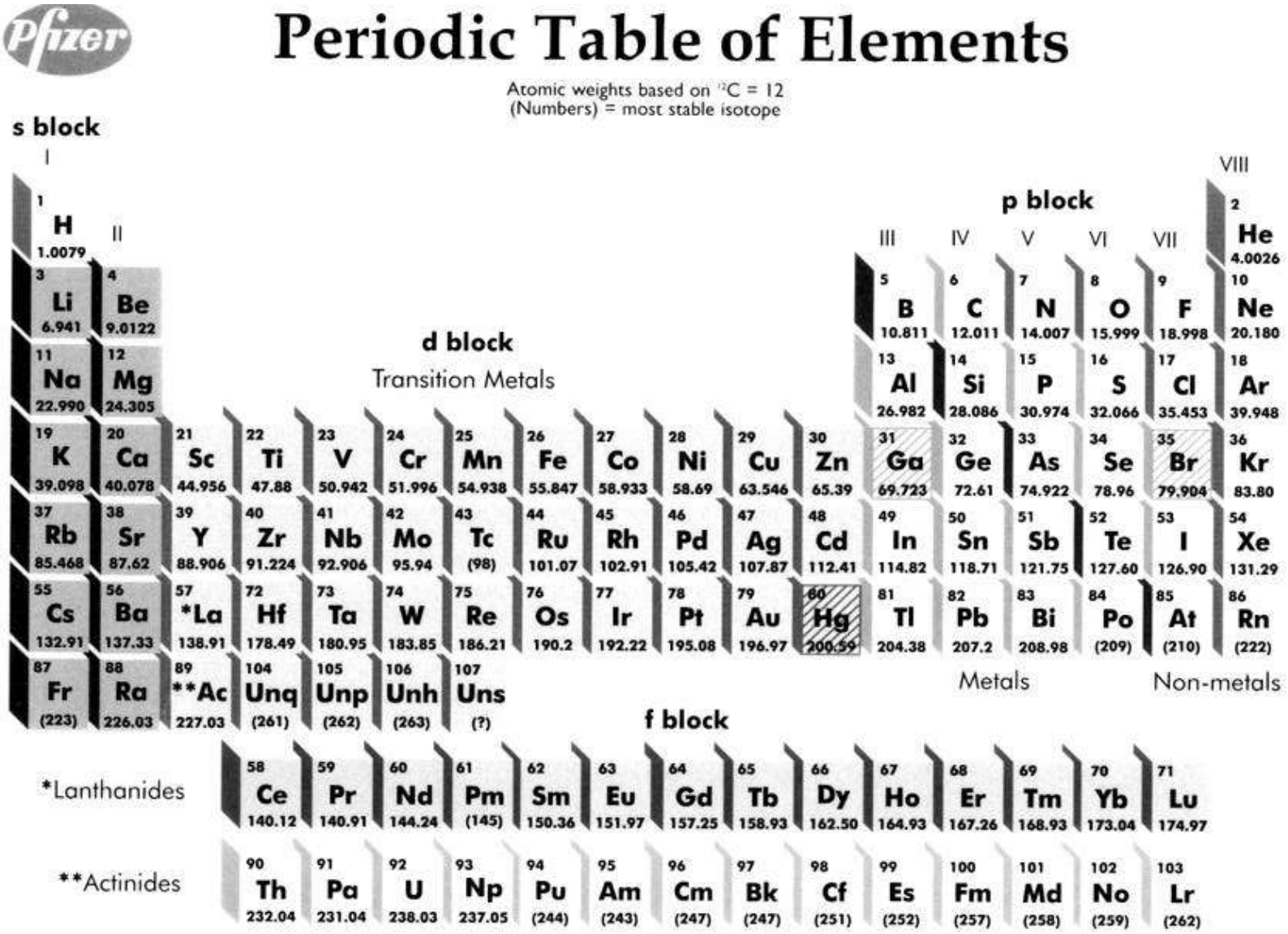


17th Chemistry Olympiad of the Baltic States

Riga, Latvia, 2009

Practical examination


Periodic Table of Elements
Atomic weights based on ¹²C = 12
(Numbers) = most stable isotope
s block
p block
d block
Transition Metals
f block
I
II
III
IV
V
VI
VII
VIII
1 H 1.0079
2 He 4.0026
3 Li 6.941
4 Be 9.0122
5 B 10.811
6 C 12.011
7 N 14.007
8 O 15.999
9 F 18.998
10 Ne 20.180
11 Na 22.990
12 Mg 24.305
13 Al 26.982
14 Si 28.086
15 P 30.974
16 S 32.066
17 Cl 35.453
18 Ar 39.948
19 K 39.098
20 Ca 40.078
21 Sc 44.956
22 Ti 47.88
23 V 50.942
24 Cr 51.996
25 Mn 54.938
26 Fe 55.847
27 Co 58.933
28 Ni 58.69
29 Cu 63.546
30 Zn 65.39
31 Ga 69.723
32 Ge 72.61
33 As 74.922
34 Se 78.96
35 Br 79.904
36 Kr 83.80
37 Rb 85.468
38 Sr 87.62
39 Y 88.906
40 Zr 91.224
41 Nb 92.906
42 Mo 95.94
43 Tc (98)
44 Ru 101.07
45 Rh 102.91
46 Pd 105.42
47 Ag 107.87
48 Cd 112.41
49 In 114.82
50 Sn 118.71
51 Sb 121.75
52 Te 127.60
53 I 126.90
54 Xe 131.29
55 Cs 132.91
56 Ba 137.33
57 *La 138.91
72 Hf 178.49
73 Ta 180.95
74 W 183.85
75 Re 186.21
76 Os 190.2
77 Ir 192.22
78 Pt 195.08
79 Au 196.97
80 Hg 200.59
81 Tl 204.38
82 Pb 207.2
83 Bi 208.98
84 Po (209)
85 At (210)
86 Rn (222)
87 Fr (223)
88 Ra 226.03
89 **Ac 227.03
104 Unq (261)
105 Unp (262)
106 Unh (263)
107 Uns (?)
Metals
Non-metals
*Lanthanides
58 Ce 140.12
59 Pr 140.91
60 Nd 144.24
61 Pm (145)
62 Sm 150.36
63 Eu 151.97
64 Gd 157.25
65 Tb 158.93
66 Dy 162.50
67 Ho 164.93
68 Er 167.26
69 Tm 168.93
70 Yb 173.04
71 Lu 174.97
**Actinides
90 Th 232.04
91 Pa 231.04
92 U 238.03
93 Np 237.05
94 Pu (244)
95 Am (243)
96 Cm (247)
97 Bk (247)
98 Cf (251)
99 Es (252)
100 Fm (257)
101 Md (258)
102 No (259)
103 Lr (262)

Introduction

General information

• Keep your safety or optical glasses on, while working in laboratory. Fill pipettes only with a bulb. Food is strongly prohibited in the laboratory.
• Participants must follow safety rules, be polite and keep instruments and your working place in neat order. Do not hesitate to ask laboratory assistant about safety.
• You can only start to work once the starting command is given.
• You are given 5 hours to complete your experimental work and fill the answer sheets. You will be notified 15 before the end of practical examination. You must stop working once the "stop" signal is given. If you are late 5 min or more, your work will be disqualified and you will be given 0 points for practical examination.
• Write your last name and code (found on your working place) in designated areas on your answer sheets.
• All results should be written in boxed areas in answer sheets. Information written in other parts of answer sheets will not be graded. Do not write on the other side of answer sheets. Ask laboratory assistant, if you need paper for calculations or clean answer sheet.
• You can only start working on the second part, when first is finished and answer sheet is turned in.
• Do not leave the laboratory without permission.
• You can only use materials given to you in the laboratory.
• Number of decimal places in calculations must be in accordance with experimental error and data analysis principles. You will be penalized for inaccurate calculations, even if your experimental skills are faultless.

Utilization of spilled chemicals and broken glassware

- All filtrates of organic compounds, washing liquids and other waste materials should be placed in waste containers.
- When disposing waste, look for the appropriate waste container.
- Broken glassware should be placed in waste basket.

Task 1
Selective reduction of highly unsaturated imine.

Sodium borohidride is selective reducing agent. In this task you will carry the condensation reaction of 3-nitroaniline and cinnamaldehyde. Water will be removed in azeotropic distillation and synthesized imine **A**, will be selectively reduced to give **B**.

Instruments and Materials:

On each workbench:
stand and clamp
hot plate
sand bath
roundbottom flask (50 cm^3)
distillation head
thermometer
Liebig condenser
bent adapter
watch glass
funnel
2 graduated cylinders (25 cm^3)
2 glass pipettes
aluminum foil
weighing paper
conical flask (25 cm^3)
2 Petri dishes
2 beakers (50 cm^3 80 cm^3)
test tube stand
3 centrifuge tubes
graduated test tube with cinnamaldehyde solution
spatula
glass rod
crystallizing dish
filter paper
chromatographic plate
for every two students
balances
scalpel
spatula
boiling stones
glass capillaries
for common use
setup for vacuum filtration
Bunsen flask with Buchner funnel
Bunsen flask with Hirsch funnel
Permanent marker

Reagents:

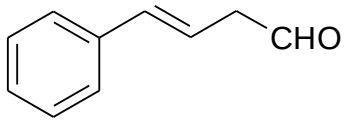
on each workbench:	**Risk and Safety phrases**
Cinnamaldehyde solution in ethanol *(in graduated test tube with ground glass stopcock)*	R36,R37,R38; S26,S36
95% ethanol	R11,R20,R21,R22,R36 ;S7,S16
distilled water	
for every two students	
3-nitroaniline	R23,R24,R25,R33,R52,R53; S28a,S36,S37,S45,S61
Sodium borohydride	R18,R22,R31,R35; S9,S14,S36,S37,S39,S45
abs. ethanol	R11,R20,R21,R22,R36, S7,S16
eluent (hexane/ethyl acetate 1:1)	R11,R38,R48/20,R62,R65,R67,R51/53; S9,S16,S29,S33,S36,S37,S61,62

Risk and Safety phrases	**Explanation**
R11	Highly flammable
R18	In use, may form flammable/explosive vapor-air mixture
R20	Harmful by inhalation
R21	Harmful in contact with skin
R22	Harmful if swallowed
R23	Toxic by inhalation
R24	Toxic in contact with skin
R25	Toxic if swallowed
R31	Contact with acids liberates toxic gas
R33	Danger of cumulative effects
R35	Causes severe burns
R36	Irritating to eyes
R37	Irritating to respiratory system
R38	Irritating to skin
R48	Danger of serious damage to health by prolonged exposure
R52	Harmful to aquatic organisms
R51	Toxic to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R62	Possible risk of impaired fertility
R67	Vapors may cause drowsiness and dizziness
S7	Keep container tightly closed
S9	Keep container in a well-ventilated place
S16	Keep away from sources of ignition
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S28a	After contact with skin, wash immediately with plenty of .water.
S29	Do not empty into drains
S36	Wear suitable protective clothing
S37	Wear suitable gloves.
S39	Wear eye/face protection

S45	In case of accident of if you feel unwell, seek medical advice immediately (show the label where possible).
S61	Avoid release to the environment. Refer to special instructions / Safety data sheets
62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label

Experiment description:

Using stand and clamp fasten 50 cm^3 round bottom flask at the appropriate height above hot plate. In order to save time, place sand bath on the hot plate, turn it on, but do not adjust heating. Using watch glass weigh 0,69 g of 3-nitroaniline and transfer through the funnel into 50 cm^3 round bottom flask. Using graduated cylinder take 10 cm^3 of absolute ethanol and add to reaction flask. Add few boiling stones. Setup distillation apparatus. Do not place thermometer in distillation head and use graduated cylinder to collect distillate. To the reaction flask, through distillation head, using pipette dropwise add all cinnamaldehyde solution (0,73 g are dissolved in 1,5 cm^3 of absolute ethanol) found in graduated test tube. Put thermometer in distillation head, cover flask with aluminum foil and start heating. While distilling, in conical flask prepare sodium borohydride solution, dissolving 0,20 g sodium borohydride in 8 – 10 cm^3 of 95 % ethanol.
Stop heating and distillation when ~ 10 cm^3 of distillate are collected. Dispose the liquid in the appropriate container. Elevate the flask, remove sand bath with hot plate, and remove bent adapter, condenser and distillation head. Transfer small amount of product from the flask into centrifuge test tube for thin layer chromatography (TLC). Dissolve obtained product in ~10 cm^3 of 95% ethanol, if necessary, stir with glass rod and heat the content. With pipette portionwise add solution of sodium borohydride to the content of the reaction flask. Keep swirling the content while adding sodium borohydride. Attach condenser to the flask and heat in the sand bath for about 20 min. *At this time you are advised to fill the answer sheet.*
Place ~15 cm^3 of water into beaker. Stop heating the reaction mixture, allow it to cool down a little and pour the content into the beaker with water. Cool in the ice bath. Filter the product in the vacuum using Buchner funnel. Save a little amount of product for TLC and recrystallize crude product from 95% ethanol. Filter recrystallized product in vacuum using Hirsch funnel. With a marker write your code on a Petri dish and place synthesized product onto it. Product samples stored in centrifuge test tubes dissolve in little amount of 95% ethanol and perform TLC.
Turn in to the laboratory assistant your Petri dish with the product, TLC plate and answer sheet.



Cinnamaldehyde

First name, last name: Code:

Task 1.

1a	1b	1c	1d	1e	task 1
10	5	5	30	10	60

a) Draw the reaction equation and IUPAC names of the compounds involved in the condensation reaction to give **A**

b) Draw the reaction equation for reduction of imine and IUPAC name of B.

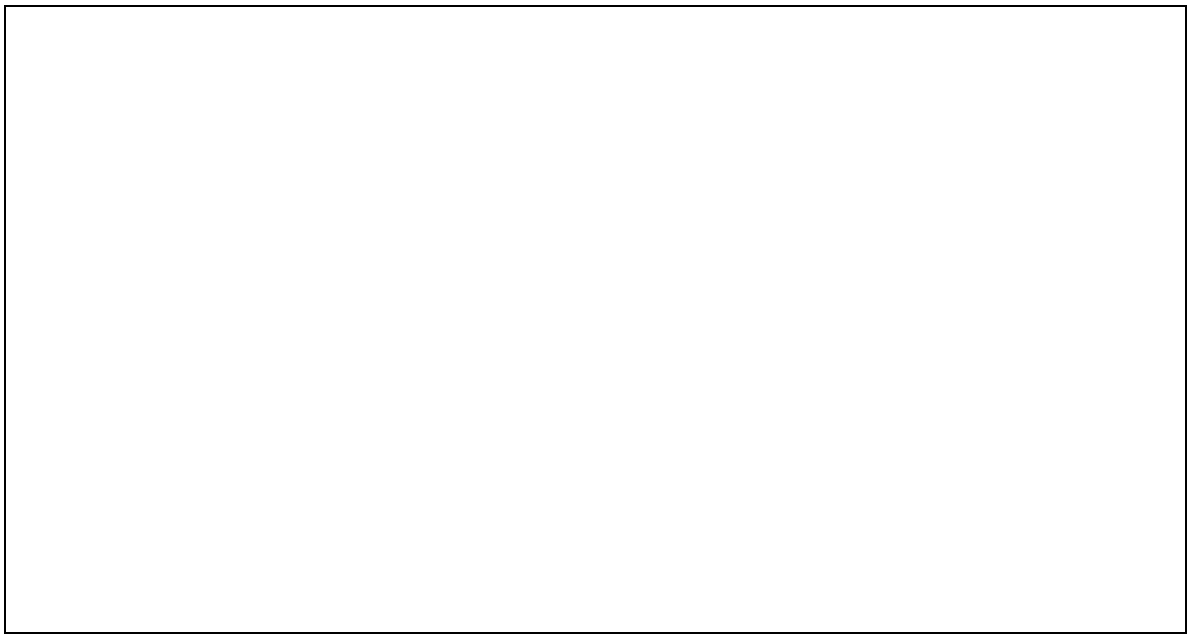
c) Theoretical yield of the product (g).

Calculations:

Theoretical yield:

d) Yield of the product (g), (to be determined by organizers):

e) Sketch the TLC plate and calculate Rf constants for compounds A and B:



Task 2.
Analysis of crystal hydrate

Sodium carbonate decahydrate loses water in dry air, but under humid conditions it absorbs water from air. Both the loss and the binding of water proceed stepwise, which results in formation of a mixture of various crystal hydrates, as a consequence, the average number of water molecules is not a positive integer.
The goal of this task is to determine the composition of a sodium carbonate sample titrating it with previously standardized solution of hydrochloric acid.

Instruments and materials:

On each workbench:
stand and clamp
hot plate
25 mL burette
funnel
50 mL beaker
thermometer
3 flatbottom flasks (250 mL)
20 mL graduated pipette
100 mL volumetric flask
funnel
stopcock
plastic pipette
wash bottle with distilled water
glass rod
filter paper
cloth for handling of hot flasks

Reagents:

On each workbench:	***Safety and Risk phrases***
0,05000 M $Na_2B_4O_7$ solution	
~ 0,1 M HCl	
Methylred indicator	
Mixed indicator (methylred and bromocresol green)	
Weighing beaker with Na_2CO_3 xH_2O sample	R36,S22,S26.

Safety and Risk phrases	***Explanation***
R36	Irritating to eyes
S22	Do not breathe dust
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

Experiment description:

On the answer sheet write the number of sodium carbonate sample and ask laboratory assistant for the mass of the sample to be analyzed.
The solution of hydrochloric acid needs to be standardized before the use. The acid is titrated with standard solution of sodium tetraborate (0,05000 M).
Transfer 20 mL of standard solution of sodium tetraborate into a flatbottom flask, add 3-5 drops of methylred indicator and titrate with hydrochloric acid solution until solution becomes pink. Write in the answer sheet the volume of the acid used. Repeat titration 2-3 times and calculate the concentration of hydrochloric acid solution.
Sodium carbonate sample quantitatively transfer from weighing beaker into 100 mL volumetric flask, dissolve in water and fill the flask until the marking. Close the flask with a stopcock and mix the content. Rinse graduated pipette with distilled water and then couple of times with prepared sodium carbonate solution. Transfer 20 mL of sodium carbonate solution into flatbottom flask; add 3-5 drops of mixed indicator. Titrate with hydrochloric acid solution until solution becomes pink. Boil the solution for about 3 minutes, then cool down to about 60 $^{\circ}$C and continue titration until solution becomes pink again. Repeat titration 3-4 times and calculate the composition of sodium carbonate crystal hydrate.

First name, last name: Code:

Task 2

2a	2b	2c	2d	2e	2.f	**Task 2**
3	1	2	3	1	10	**20**

The number of sodium carbonate crystal hydrate sample:

Weight of the sample:

a) Volume of hydrochloric acid solution used in titration of sodium tetraborate solution (mL)

1.

2.

3.

4.

Average volume:

b) Reaction equation:

c) Calculations of the concentration of hydrochloric acid solution

d) Volume of hydrochloric acid solution used in titration of sodium carbonate solution (mL)

1.

2.

3.

4.

Average volume:

e) Reaction equation

f) Calculations of the composition of sodium carbonate crystal hydrate:

Determined formula: