BChO 2022

Practical Exam

April 21, 2022
Vilnius, Lithuania

Atomic number → 1 ← Atomic weight: 1.00794 ← **Atomic symbol**: H ← Covalent radius, Å: 0.28

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**1** 1.00794 **H** 0.28																	**2** 4.00260 **He** 1.40
2	**3** 6.941 **Li**	**4** 9.01218 **Be**											**5** 10.811 **B** 0.89	**6** 12.011 **C** 0.77	**7** 14.0067 **N** 0.70	**8** 15.9994 **O** 0.66	**9** 18.9984 **F** 0.64	**10** 20.1797 **Ne** 1.50
3	**11** 22.9898 **Na**	**12** 24.3050 **Mg**											**13** 26.9815 **Al**	**14** 28.0855 **Si** 1.17	**15** 30.9738 **P** 1.10	**16** 32.066 **S** 1.04	**17** 35.4527 **Cl** 0.99	**18** 39.948 **Ar** 1.80
4	**19** 39.0983 **K**	**20** 40.078 **Ca**	**21** 44.9559 **Sc**	**22** 47.867 **Ti** 1.46	**23** 50.9415 **V** 1.33	**24** 51.9961 **Cr** 1.25	**25** 54.9381 **Mn** 1.37	**26** 55.845 **Fe** 1.24	**27** 58.9332 **Co** 1.25	**28** 58.6934 **Ni** 1.24	**29** 63.546 **Cu** 1.28	**30** 65.39 **Zn** 1.33	**31** 69.723 **Ga** 1.35	**32** 72.61 **Ge** 1.22	**33** 74.9216 **As** 1.20	**34** 78.96 **Se** 1.18	**35** 79.904 **Br** 1.14	**36** 83.80 **Kr** 1.90
5	**37** 85.4678 **Rb**	**38** 87.62 **Sr**	**39** 88.9059 **Y**	**40** 91.224 **Zr** 1.60	**41** 92.9064 **Nb** 1.43	**42** 95.94 **Mo** 1.37	**43** (97.905) **Tc** 1.36	**44** 101.07 **Ru** 1.34	**45** 102.906 **Rh** 1.34	**46** 106.42 **Pd** 1.37	**47** 107.868 **Ag** 1.44	**48** 112.41 **Cd** 1.49	**49** 114.818 **In** 1.67	**50** 118.710 **Sn** 1.40	**51** 121.760 **Sb** 1.45	**52** 127.60 **Te** 1.37	**53** 126.904 **I** 1.33	**54** 131.29 **Xe** 2.10
6	**55** 132.905 **Cs**	**56** 137.327 **Ba**	**57-71** **La-Lu**	**72** 178.49 **Hf** 1.59	**73** 180.948 **Ta** 1.43	**74** 183.84 **W** 1.37	**75** 186.207 **Re** 1.37	**76** 190.23 **Os** 1.35	**77** 192.217 **Ir** 1.36	**78** 195.08 **Pt** 1.38	**79** 196.967 **Au** 1.44	**80** 200.59 **Hg** 1.50	**81** 204.383 **Tl** 1.70	**82** 207.2 **Pb** 1.76	**83** 208.980 **Bi** 1.55	**84** (208.98) **Po** 1.67	**85** (210) **At**	**86** (222.02) **Rn** 2.20
7	**87** (223) **Fr**	**88** (226.03) **Ra** 2.25	**89-103** **Ac-Lr**	**104** (261.11) **Rf**	**105** (262.11) **Db**	**106** (263.12) **Sg**	**107** (262.12) **Bh**	**108** (265) **Hs**	**109** (266) **Mt**	**110** (271) **Ds**	**111** (272) **Rg**	**112** (285) **Cn**	**113** (284) **Nh**	**114** (289) **Fl**	**115** (288) **Mc**	**116** (293) **Lv**	**117** (294) **Ts**	**118** (294) **Og**

57 138.906 **La** 1.87	**58** 140.115 **Ce** 1.83	**59** 140.908 **Pr** 1.82	**60** 144.24 **Nd** 1.81	**61** (144.91) **Pm** 1.83	**62** 150.36 **Sm** 1.80	**63** 151.965 **Eu** 2.04	**64** 157.25 **Gd** 1.79	**65** 158.925 **Tb** 1.76	**66** 162.50 **Dy** 1.75	**67** 164.930 **Ho** 1.74	**68** 167.26 **Er** 1.73	**69** 168.934 **Tm** 1.72	**70** 173.04 **Yb** 1.94	**71** 174.04 **Lu** 1.72
89 (227.03) **Ac** 1.88	**90** 232.038 **Th** 1.80	**91** 231.036 **Pa** 1.56	**92** 238.029 **U** 1.38	**93** (237.05) **Np** 1.55	**94** (244) **Pu** 1.59	**95** (243.06) **Am** 1.73	**96** (247.07) **Cm** 1.74	**97** (247.07) **Bk** 1.72	**98** (251.08) **Cf** 1.99	**99** (252.08) **Es** 2.03	**100** (257.10) **Fm**	**101** (258.10) **Md**	**102** (259.1) **No**	**103** (260.1) **Lr**

Constants and Formulae

Avogadro's constant, $N_A = 6.0221\times10^{23}$ mol^{-1}

Boltzmann constant, $k_B = 1.3807\times10^{-23}$ J K^{-1}

Universal gas constant, $R = 8.3145$ J K^{-1} mol^{-1} = 0.08205 atm L K^{-1} mol^{-1}

Speed of light, $c = 2.9979\times10^{8}$ m s^{-1}

Planck's constant, $h = 6.6261\times10^{-34}$ J s

Faraday constant, $F = 9.64853399\times10^{4}$ C

Mass of electron, $m_e = 9.10938215\times10^{-31}$ kg

Standard pressure, P = 1 bar = 10^5 Pa

Atmospheric pressure, $P_{atm} = 1.01325\times10^{5}$ Pa = 760 mmHg = 760 torr

Zero of the Celsius scale, 273.15 K

1 picometer (pm) = 10^{-12} m; 1 Å = 10^{-10} m; nanometer (nm) = 10^{-9} m

1 eV = 1.6×10^{-19} J

1 amu = $1.66053904 \times 10^{-27}$ kg

Ideal gas equation: $PV = nRT$

Enthalpy: $H = U - PV$

Gibbs free energy: $G = H - TS$ $\qquad \Delta G = \Delta G^o + RT\ln Q$

$$\Delta G^o = -RT\ln K = -nFE^o_{cell}$$

Entropy change: $\Delta S = \frac{q_{rev}}{T}$, where q_{rev} is heat for the reversible process

$\Delta S = nR\ln\frac{V_2}{V_1}$ (for isothermal expansion of an ideal gas)

Nernst equation: $E = E^o + \frac{RT}{nF}\ln\frac{C_{ox}}{C_{red}}$

Energy of a photon: $E = \frac{hc}{\lambda}$ $\qquad$ Lambert-Beer law: $A = \log\frac{I_0}{I} = \varepsilon bC$

Integrated rate law

Zero order $[A] = [A]_0 - kt$ $\qquad$ First order $\ln[A] = \ln[A]_0 - kt$

Second order $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Arrhenius equation $k = Ae^{-E_a/RT}$

General Directions

- Follow safety rules. No eating or drinking in the lab. Always wear your lab coat and safety goggles when being in the lab. Ask your lab assistant for the gloves.
- Write your name and student code on each page of the answer sheets.
- We suggest to start from the first task.
- During the Practical exam, some of the glassware and plastics are expected to be used several times. Clean it carefully.
- You have 5 hours to work on the exam problems. **Begin** only when the **START** command is given.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded.
- You must **stop** working when the **STOP** command is given.
- Do not leave your seat until permitted by the supervisors.
- The official English version of this examination is available on request only for clarification.

Practical task #1

Let's brominate!

20 points

It hurts your head - take aspirin. Such advice can be heard from the grandmother when you have a headache, or your body temperature rises. The chemical name of aspirin, acetylsalicylic acid, clearly indicates the relationship of aspirin with another chemical compound, salicylic acid (chemical name: 2-hydroxybenzoic acid). More than two thousand years ago, people knew that willow bark extract has excellent properties - it reduces pain and fever. And now we know why. This efficacy of this extract is determined by salicin, a derivative of salicylic acid that is similar in structure to aspirin. Salicin was expensive to extract from willow bark, so in the second half of 19th century chemists learned how to synthesize pure salicylic acid in the hope that it would have similar properties to salicin. However, the consumption of salicylic acid has caused a number of harmful side effects such as stomach irritation or even deafness. At the end of the 19th century, Bayer launched a synthetic drug made from salicylic acid that provides excellent pain relief and temperature reduction without causing serious side effects. We still know this drug as aspirin.

Fortunately, salicylic acid (its water solubility is 2.48 g/L at 25^{0}C) was not just an unsuccessful attempt to imitate nature. It found another application. Nowadays, it is used in the form of an alcoholic solution for external use on the skin. Salicylic acid has excellent skin disinfectant properties and is therefore used to treat a variety of skin conditions.

As an extremely curious chemist, I found it very interesting to explore how much of that active ingredient is in that willow bark. So, using all my talents and the skills I gained during my long hours in the laboratory, I took a small piece of willow bark, boiled its extract and made sodium salicylate (the sodium salt of salicylic acid) from this extract through various chemical reactions and put it all into a beaker for you. It is your task to determine by titration how many milligrams of sodium salicylate (its molar mass is 160.1 g/mol) are in this beaker.

Dear Chemist, for this purpose, I propose to you to use the wonderful bromination reaction of salicylic acid and the subsequent method of iodometric titration analysis. Salicylic acid is known to react with bromine in a ratio of 1:3.

In this work, the bromine required for the bromination reaction is prepared in the reaction mixture by reacting the bromate ions with the bromide ions. It is known that 3 moles of bromine are formed from 1 mole of bromate ions.

Chemicals for personal use:

Chemical	Concentration	Label
$KBrO_3$ solution	0.0300 M	**0.0300 M $KBrO_3$**
KBr solution	0.4 M	**0.4 M KBr**
$Na_2S_2O_3$ solution	0.0500 M	**0.0500 M $Na_2S_2O_3$**
H_2SO_4 solution	1 M	**1 M H_2SO_4**
Sodium salicylate	-	**(Your working place number)**

Chemicals for general use:

Chemical	Place	Label
Potassium iodide KI	near balances	**KI**
Starch indicator	on the shelf, next to your working place	**Starch indicator**

Labware and equipment:

Burette	1
Laboratory stand with a clamp	1
Hotplate (in the fume hood)	1
Balances (for general use)	1
Glass funnel	1
Erlenmeyer flask for titration	1
Measuring cylinder	1
50 mL beaker (with sodium salicylate inside)	1
10.00 mL volumetric pipette	2
Parafilm squares	4
Distilled water wash bottle (for both practical tasks)	1
Glass rod	1
Pasteur pipette	2
50.00 mL measuring flask with a cap	1
Rubber bulb for the pipette	1
Weighing boat	1
Safety goggles (for both practical tasks)	1
Waste beaker (for both practical tasks)	1

Notes:

1. When working with solids, it is highly recommended not to wear protective gloves due to the possible electrostatic charging of solids.
2. If you need additional sample of sodium salicylate, we will unfortunately have to deduct 2 points from your final evaluation for this practical task.
3. If you break or damage something from your labware or equipment and need a replacement, 1 point will be deducted from your final evaluation for this practical task.
4. Hotplates in the fume hoods are for general use.

Good luck!

Part 1. Practical part

Procedure:

1. Prepare 50.00 mL of aqueous sodium salicylate solution in a measuring flask. Use all the sodium salicylate provided in a 50 mL beaker for this purpose. Be careful and pay attention to the volumes in this step. The 50.00 mL sodium salicylate solution you have prepared will be called as the test solution later on in this practical task.
2. Add 10.00 mL of test solution and 10.00 mL of $KBrO_3$ solution to an Erlenmeyer flask with a volumetric pipette. Add 10 mL of KBr solution and 10 mL of distilled water to the same flask with a measuring cylinder. Mix the contents of the flask well by swirling the flask.
3. Using a measuring cylinder, measure 10 mL of 1 M H_2SO_4 solution and using Pasteur pipette transfer it very slowly, in very small portions, to the same Erlenmeyer flask over 3 minutes. Stir the solution in the conical flask continuously by swirling the flask throughout whole process. When the acid addition is complete, the solution in the flask may become cloudy.
4. After transferring all the acid to the conical flask, cover it quickly and tightly using a square of paraffin film. Do this as soon as possible and then mix the contents of the flask by swirling it for about another minute until it turns yellow and you start seeing a cloudy liquid.
5. Then wrap the flask in towel paper (to protect from light), place it in a fume cupboard on a warm hotplate (do NOT adjust hotplate settings!), and leave it there for 30 minutes to allow all the reactions to take place. Occasionally stir the contents of the flask by swirling it.
6. Then weigh 0.5 g of solid KI, remove the parafilm from the conical flask, add KI to the flask IN THE FUME HOOD and mix well until dissolved. Once KI is in the flask, you can take it out from the fume cupboard to your workplace. Titrate the mixture in the conical flask with $Na_2S_2O_3$ solution. The color of the mixture becomes brighter during titration. When the color of the solution is light yellow, add about 1 mL of starch indicator and continue adding the thiosulfate solution dropwise until the solution is colorless and does not turn blue 15-20 seconds after the last drop.
7. Record the titration data on the answer sheet. If necessary, repeat the entire procedure from step 2 as many times as you think it is necessary.

Part 2. Theoretical part

1. Draw the structures of salicylic acid and sodium salicylate.
2. From the following statements (on the answer sheets) choose the one which best describes why it is better to use sodium salicylate for this analysis instead of salicylic acid and it would be very difficult or even impossible to perform exactly the same analysis if salicylic acid was used?
3. After adding the acid, you may notice that after a while the liquid in the flask started to turn yellow, and after 30 minutes it could be observed that even the air in the flask above the liquid has a brownish tinge. Write the balanced complete equation for the reaction that caused this color to occur and identify the substance itself.
4. After potassium iodide addition, the entire contents of the flask suddenly became dark. Write the balanced complete equation of the reaction that took place.
5. When titrating the mixture in the flask with sodium thiosulphate, the thiosulphate ions are oxidized to tetrathionate ions and the reaction $2S_2O_3^{2-}$ $S_4O_6^{2-} + 2e^-$ takes place. The other particles in the flask are reduced. Write the balanced complete equation of the reaction which takes place by titrating the contents of the flask with sodium thiosulphate solution.
6. Calculate how much sodium salicylate has been added to the beaker.
7. If you sealed the flask really well with parafilm during the bromination reaction, you may notice that when the flask was left for 30 minutes in the fume cupboard, the film slightly distended, which means that the volume of the substances in the flask increased. During the bromination reaction of salicylic acid, a gaseous product is generated, which is one of the reasons why parafilm has distended. Identify that gaseous product.
8. During the bromination reaction of salicylic acid, white precipitate forms in the flask, which is the product of the bromination reaction. The structural formulas of several compounds are given on the answer sheets. Choose from them and circle the formula of the bromination reaction product (mark on the answer sheets).

Practical task #2

Investigation of solutions of unknown composition

20 points

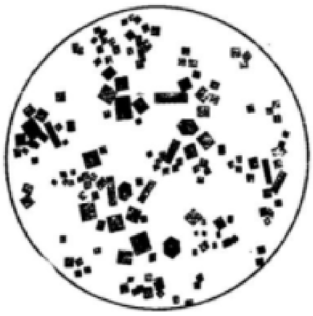
The goal of this task is to identify what ions are in three solutions given to you. They can have any combination of these ions: K^+; NH_4^+; Ca^{2+}; Ba^{2+}. Every ion has a specific reaction to identify it. Here's few of them:

Tests for NH_4^+ ions:

1. Add 6 M NaOH to the solution of NH_4^+ ions. Put a moist red litmus paper over the opening of the test tube and put the tube into the water bath. The paper changes its' colour.
2. Nessler reagent ($K_2[HgI_4]$ + KOH) in solutions of ammonium salts form reddish brown precipitates. If solution is strongly acidic Nessler reagent can decompose and form red HgI_2 precipitates. Because of it, it's easy to falsely identify NH_4^+ even if they're not in the solution.

Test for K^+ ions:

Add a drop of unknown solution and a drop of $Na_2Pb[Cu(NO_2)_6]$ onto the microscope slide. Connect the drops with glass rod. If K^+ ions are presented after waiting for 1-2 min, black cube shaped crystals can be observed under the microscope:



Attention! NH_4^+ ions also form crystals so if NH_4^+ is identified in the unknown solution it must be removed. To do this, add 10-13 drops of formaldehyde to a test tube with 5-7 drops of unknown solution. This reaction fully eliminates NH_4^+ ions from the solution.

Attention! After a reaction with formaldehyde the test tube can seem fogged. This kind of tube can be given to the laboratory assistant to be changed to a new one (points won't be deducted for it).

You should find a way to test for Ca^{2+} and Ba^{2+} ions on your own.

Tips:

1. Try all the reactions with solutions of known composition.
2. In unknown solutions some ions can interfere with identification of other components of the solution so it's useful to separate some ions from the others. If right reagents are selected specific ions can be precipitated. Decanting smoothly can be complicated so usage of the centrifuge is advised. After centrifuging the sediment is in the bottom of the tube and liquid can be poured out easily.

3. Prepare a scheme how the composition of the solution should be investigated and try it out on the mixture that you made yourself by mixing known solutions.
4. Success of the analysis is highly dependent on how clean the labware is, so it is recommended to thoroughly clean any equipment with tap water and rinse it a few times with distilled water.

Chemicals for personal use:

Chemical	Label
3 solutions for analysis	**XX.1; XX.2; XX.3 (XX – your workplace number)**
Litmus paper	**-**

Chemicals for general use:

Chemical	Place	Label
NH_4NO_3 (aq)	On the shelf, next to your working place	**NH_4^+**
KCl (aq)	On the shelf, next to your working place	**K^+**
$Ca(NO_3)_2$ (aq)	On the shelf, next to your working place	**Ca^{2+}**
$Ba(NO_3)_2$ (aq)	On the shelf, next to your working place	**Ba^{2+}**
6 M NaOH	In the fume hood	**6 M NaOH**
$K_2[HgI_4]$ + KOH (aq)	In the fume hood	**Nessler reagent**
$Na_2Pb[Cu(NO_2)_6]$ (aq)	Next to the microscope	**$Na_2Pb[Cu(NO_2)_6]$**
Formaldehyde	In the fume hood	**Formaldehyde**
2 M CH_3COOH	In the test tube rack	**2 M CH_3COOH**
2 M H_2SO_4	In the test tube rack	**2 M H_2SO_4**
2 M $(NH_4)_2CO_3$	In the test tube rack	**2 M $(NH_4)_2CO_3$**
2 M $(NH_4)_2C_2O_4$	In the test tube rack	**2 M $(NH_4)_2C_2O_4$**
2 M K_2CrO_4	In the test tube rack	**2 M K_2CrO_4**

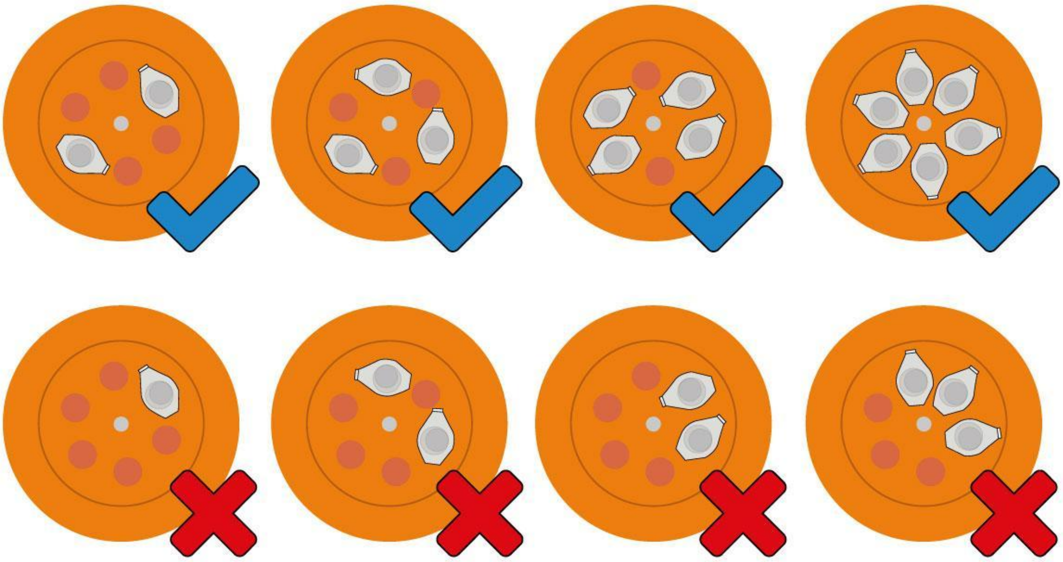
Labware and equipment:

Plastic tubes	8
Stand for plastic tubes	1
Glass rod	1
Glass Pasteur pipette	1
Microscope slides	1
Centrifuge (for general use)	
Water bath (for general use)	
Microscope (for general use)	

Instructions:

How to use the centrifuge:

1. Open the lid of the centrifuge.
2. Put test tubes into the centrifuge in the way that weight would be equally divided.



Picture taken from https://bento.bio/protocol/biotechnology-101/centrifuge-intro/

3. If there is only one test tube that need centrifuging counterweight must be added (test tube with mark “X” on it, next to the centrifuge).
4. Make sure to note where the tube was in the centrifuge (spaces are marked with numbers).
5. Close the lid and press until you hear a click.
6. Press “START” button.

Ask the lab assistant if help is needed.

How to use the microscope:

1. Use the yellow lens.
2. Put the microscope slide under it.
3. Look at the tray on which the slide lies (**not through the ocular!**) and turn a bigger black nob (marked in the photo) so the tray would be lifted close to lens (**do not dip the lens into the solution!**).

4. Look through the ocular and slowly lower down the tray until the view becomes clear.

Note: If lens was dipped into the solution – inform the laboratory assistant immediately (points won't be deducted for it).

Evaluation:

Points are deducted for:

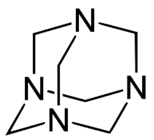
1. Every time when unknown solution needs to be refilled (marked XX.1 – XX.3).
2. Every time when broken glassware needs to be replaced.

Points are not deducted for:

1. Asking to refill any other solution.
2. Asking to refill litmus paper.
3. Asking to replace the tube fogged by formaldehyde reaction.
4. Asking to refill distilled water.

Results and theoretical part

1. Write down the number of the tube and what cations were found in the solution.
2. Write down the equation that explains why it is important to moisturise the litmus paper before trying to identify the NH_4^+ ions.
3. Balanced short ionic equation for reaction between Nessler reagent and NH_4^+ ions looks like this: $NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \rightarrow X + 7Y^- + 3Z$. Write chemical formula of X, Y^- and Z.
4. Write the equation of KCl and $Na_2Pb[Cu(NO_2)_6]$ reaction.
5. When NH_4^+ ions react with formaldehyde urotropine is formed. Unbalanced reaction scheme:
$NH_4^+(aq)$ + Formaldehyde $\rightarrow$ Urotropine (aq) + A^+ (aq) + B (l)

Urotropine - 

Write and balance the reaction equation.