56th INTERNATIONAL MENDELEEV CHEMISTRY OLYMPIAD

May 9–16, 2022

Tashkent, Uzbekistan



PRACTICAL EXAM

Name Surname	
Country	
Student Code	
Seat No.	

Tashkent 2022

General directions

1. Wearing your lab coat and goggles (or your own correcting ones) is obligatory during the whole experimental exam.
2. Take care when handling the acid and alkali solutions!
3. Fill pipettes using a three-way bulb only. It is absolutely prohibited to suck solutions into the pipette using your mouth.
4. The amounts of the provided solutions are limited. A spilled or completely used up solution will be replaced with a penalty.
5. Work with burettes:

   a) You are provided with clean, dry pipettes and burettes. **Do not spend the solutions for rinsing them** on first use.

   b) You are given burettes with open stopcocks. Close the burette stopcock before use.

   c) If an air bubble remains in the tip when filling the burette, gently shake the burette in an upright position. If it doesn't help, contact a lab assistant.

   d) Burette stopcocks may mildly leak. Use a 50 ml beaker under the burette.
6. Pour the used solutions into the plastic beaker for waste. If it is full, contact a lab assistant.
7. For your convenience, some workplaces are separated by white markings. When completing the exam, do not interfere with other Olympiad participants. Keep your working place in order.
8. If you have broken something, ask your lab assistant, who will help you dispose the glassware and provide you with the substitute.
9. Use the backside of the booklet sheets for your draft work.
10. The total duration of the exam is 5 hours. After the STOP command, you must immediately stop your work and hand over all the pages to your lab assistant.

Chemicals and equipment

For each participant	*Quantity*	*Label*
Protective goggles	1	
Paper towels	1 roll	
Solid waste container (on the floor)	1	
1 L container for waste solutions	1	
Wash bottle with distilled water	1	**H_2O dist.**
50 mL beaker	2	
150 mL beaker	2	
250 mL beaker	1	
Glass rod	1	
Lab steel stand	1	
Steel clamp for the lab stand	1	
Retort ring for filter funnel	1	
2 burettes clamp	1	
25 mL burette	2	
125 mL conical flask for titration	3	
Filter paper	6	
Glass filter funnel, 75 mm diameter	1	
10 mL volumetric pipette	2	
$Pb(NO_3)_2$ solution, see the exact concentration on the label	30 mL	**$Pb(NO_3)_2$ X.XX M**
KI solution, see the exact concentration on the label	35 mL	**KI X.XX M**
Test tube rack	1	
Non-graduated test tubes (numbered)	9	**1–9**
10 mL graduated pipette	1	
5 mL graduated pipette	2	
Three-way bulb	1	
$Ca(NO_3)_2$ solution, unknown concentration	13 mL	**$Ca(NO_3)_2$ with a seat number**
Standard KIO_3 solution, 0.2210 M (in a 100 mL volumetric flask)	~95 mL	**KIO_3**
Standard Na_2EDTA solution, 0.0238 M	80 mL	**Na_2EDTA**
NaOH solution, 2 M	15 mL	**NaOH**
Murexide mixed with NaCl, 1% w/w	3 g	**Murexide**
Plastic spatula for the indicator mixture	1	
HCl solution, 1 M	15 mL	**HCl 1 M**
KI solution, 5% w/w	80 mL	**KI 5%**
Starch solution, 0.5% w/w	10 mL	**Starch**
Standard $Na_2S_2O_3$ solution, 0.0947 M	80 mL	**$Na_2S_2O_3$**
25 mL graduated cylinder for KI	1	
10 mL graduated cylinder for HCl, NaOH	2	
Watch glass	2	
Aluminium foil, 25×20 cm	2	
Solid $Ca(OH)_2$	~13 g	**$Ca(OH)_2$**
Standard HCl solution, 0.0300 M	200 mL	**HCl 0.0300 M**
Indicator bromothymol blue	10 mL	**BTB**
50 mL reagent bottle with screw cap	3	**3A**, **3B** and **3C**
Thermometer 0–100 ˚C	1	
Ruler	1	

On a shared table or in the fume hood

Standard KIO_3 solution in a dropper bottle, 0.2210 M	100 mL	**KIO_3**
Water (60–70°C) in a beaker on a heating plate	2 L	
Water (80–90°C) in a beaker on a heating plate	2 L	
Latex protective gloves	1 pack	
Marker	2	

Shared equipment (per laboratory)

Heating plate	1
Clock	1

To dissolve or not to dissolve

Part 1. Lead iodide PbI_2

In the first part of the exam, you will perform a semi-quantitative determination of the solubility product of lead iodide by making solutions with different lead and iodide concentrations. Precipitation can be considered as establishment of the precipitate – solution equilibrium.

In 9 numbered dry test tubes (*you are provided with clean test tubes, no need to wash or rinse them with water*), mix the reagents in the following order: water, KI, and $Pb(NO_3)_2$. Volumes are given in the table below. Calculate the water volumes yourself so that the total volume of each solution in the test tubes is equal to 10.00 mL. Please note that the pipettes provided may be graduated to the tip or not. Thoroughly stir the solutions with the glass rod and rub it against the walls of the test tubes. Use clean and dry glass rod for each test tube. Leave the test tubes for 15 minutes aside to reach the equilibrium. After that, note in which test tubes a precipitate has formed.

Write down the concentrations of given KI and $Pb(NO_3)_2$ solutions:

c(KI) = _____ M $c(Pb(NO_3)_2)$ = _____ M.

Test tube	H_2O volume, mL	KI solution volume, mL	$Pb(NO_3)_2$ solution volume, mL	Precipitation (+/–)
1		1.00	1.00	
2		2.00	1.00	
3		4.50	1.50	
4		2.00	2.00	
5		5.00	2.00	
6		1.00	2.50	
7		2.50	3.00	
8		5.00	3.00	
9		5.00	4.00	

Questions

1.1. Write down the expression for the solubility product (K_{sp}) of lead iodide using equilibrium concentrations [Pb^{2+}] and [I^-], and the chemical expression of the equilibrium corresponding to this constant:

1.2. For each test tube, calculate the concentrations of the lead and iodide ions ($c(Pb^{2+})$ and $c(I^-)$, respectively) in the solutions immediately after preparation. For the calculation, ignore the precipitation if it occurs. Calculate and write down the values of Q, which are expressed in the same way as K_{sp}, but with the calculated concentrations instead of the equilibrium ones.

Test tube	$c(Pb^{2+})$, M	$c(I^-)$, M	Q
1			
2			
3			
4			
5			
6			
7			
8			
9			

1.3. Based on the experiment results, conclude the K_{sp} range of the precipitate:

_____ < K_{sp} < _____

Part 2. Calcium iodate $Ca(IO_3)_2$

In this section, the solubility product of calcium iodate is to be determined. For this, you will mix the solutions of calcium salt of an unknown concentration and potassium iodate, separate the precipitate and determine the content of calcium and iodate ions in the saturated solution using complexometric and iodometric titrations. Besides, you will need to quantify the concentration of the calcium salt in the initial solution.

Part 2a. Preparation of $Ca(IO_3)_2$ saturated solution

Fill the 100 mL volumetric flask to the mark with the standard 0.2210 M KIO_3 solution using the dropper bottle with the identical KIO_3 solution located on the shared table. Fully transfer the prepared solution to the dry 250 mL beaker (*do not rinse the volumetric flask with water!*) and add 10.00 mL of the $Ca(NO_3)_2$ solution with a volumetric pipette. Thoroughly stir the mixture with the clean and dry glass rod. The white precipitate of $Ca(IO_3)_2$ must form.

Stir the suspension periodically for precisely 10 minutes and filter it through a dry filter paper in a dry 150 mL beaker. It is essential that the beaker, filter paper and the filter funnel are initially dry, and the filtrate is a transparent saturated solution (do not wash the precipitate with water).

Part 2b. Complexometric determination of $[Ca^{2+}]$ in the filtrate

Prepare the burette (*you are initially provided with clean and dry burettes, there is no need to rinse them with a filling solution on the first use*) and fill it with the standard Na_2EDTA solution.

Put 10.00 mL of the filtrate into a conical flask for titration using a volumetric pipette. Add 2 mL of 2 M NaOH with a cylinder, then 15–20 mL of water, mix it, and add 1–2 spatulas of the murexide indicator. Mix well and titrate with the standard 0.0238 M Na_2EDTA solution until the stable change of the colour from light pink to violet.

Repeat the titration as needed. Write down the results in the table:

Burette readings, mL		The volume of Na_2EDTA solution spent on titration, mL
Initial	Final	

Accepted volume of Na_2EDTA: _____ mL

Questions

2.1. Calculate the concentration $[Ca^{2+}]$ in the filtrate:

$[Ca^{2+}]$ = _____ M

Part 2c. Iodometric determination of $[IO_3^-]$ in the filtrate

Prepare a clean burette or rinse the previously used one with distilled water and a small portion of the $Na_2S_2O_3$ standard solution. Fill it up with the same solution.

Put 10.00 mL of the filtrate into a clean conical flask for titration using a volumetric pipette. Add 2 mL of 1 M HCl, then 20 mL of the KI solution with cylinders, and stir the mixture. Cover the flask with a watch glass, wrap it up with a piece of foil to protect from light, and leave aside for 3–5 minutes.

Titrate the mixture with the standard 0.0947 M $Na_2S_2O_3$ solution to pale yellow colour. Add a few drops of the starch solution and continue the titration until discolouration of the solution.

Repeat the titration as needed. Write down the results in the table:

Burette readings, mL		The volume of $Na_2S_2O_3$ solution spent on titration, mL
Initial	Final	

Accepted volume of $Na_2S_2O_3$: _____ mL

Questions

2.2. Write down the reaction equation between the iodate and iodide ions in an acidic medium:

2.3. Write down the equation of a reaction which occurs during the titration with the thiosulfate ions:

2.4. Calculate the concentration $[IO_3^-]$ in the filtrate:

$[IO_3^-]$ = _____ M

2.5. Calculate $K_{sp}(Ca(IO_3)_2)$:

$K_{sp}(Ca(IO_3)_2)$ = _____

2.6. Calculate the concentration of $Ca(NO_3)_2$ in the initial solution (in the reagent bottle):

$c(Ca(NO_3)_2)$ = _____ M

2.7. What is the mass of $Ca(IO_3)_2$ precipitated by mixing the initial solutions?

$m(Ca(IO_3)_2)$ = _____ g

Part 3. Calcium hydroxide $Ca(OH)_2$

In the final section of the exam, you are suggested to determine the thermodynamic parameters (ΔH^0 and ΔS^0) of the calcium hydroxide dissolution by analysing its solubility at different temperatures using the acid-base titration of saturated solutions.

Part 3a. Determination of K_{sp} at room temperature

Prepare a clean burette or rinse the previously used one with distilled water and a small portion of the HCl standard solution. Fill it up with the same solution.

Pour ca. 50 mL of distilled water in a 150 mL beaker. Add 2–3 spatulas of $Ca(OH)_2$, stir for no more than 1 minute and record the temperature of the mixture. Filter the non-dissolved $Ca(OH)_2$ using a clean and dry filter paper and a funnel. It is essential that the filter paper and the filter funnel are initially dry; do not wash the precipitate with water. Collect the filtrate in the clean and dry reagent bottle «**3A**». Put 10.00 mL of the filtrate into a clean conical flask for titration and close the bottle with the filtrate with a screw cap (do not leave the bottle with the filtrate open). Add 3 drops of the bromothymol blue solution («**BTB**») and titrate with the standard 0.0300 M HCl solution.

Repeat the titration as needed. Note that it is important to perform the titration directly after taking the aliquot. Write down the results in the table:

Burette readings, mL		The volume of HCl solution spent on titration, mL
Initial	Final	

Temperature of the mixture: _____°C Accepted volume of HCl: _____ mL

Part 3b. Determination of K_{sp} at temperature 45–55°C

Ask the lab assistant to pour ca. 50 mL of hot water of the required temperature in your 150 mL beaker. Immerse the thermometer in the water and let it cool down to 45–55°C. Rapidly add 2–3 spatulas of $Ca(OH)_2$, stir for no more than 1 minute and record the temperature of the mixture. Perform the filtration and titration as in Part 3a, collecting the filtrate in the clean and dry reagent bottle «**3B**». Write down the results in the table:

Burette readings, mL		The volume of HCl solution spent on titration, mL
Initial	Final	

Temperature of the mixture: _____°C Accepted volume of HCl: _____ mL

Part 3c. Determination of K_{sp} at temperature 65–75°C

Repeat the experiment from Part 3b at a water temperature of 65–75°C. In this case, collect the filtrate in the clean and dry reagent bottle «**3C**». Write down the results in the table:

Burette readings, mL		The volume of HCl solution spent on titration, mL
Initial	Final	

Temperature of the mixture: _____°C Accepted volume of HCl: _____ mL

Questions

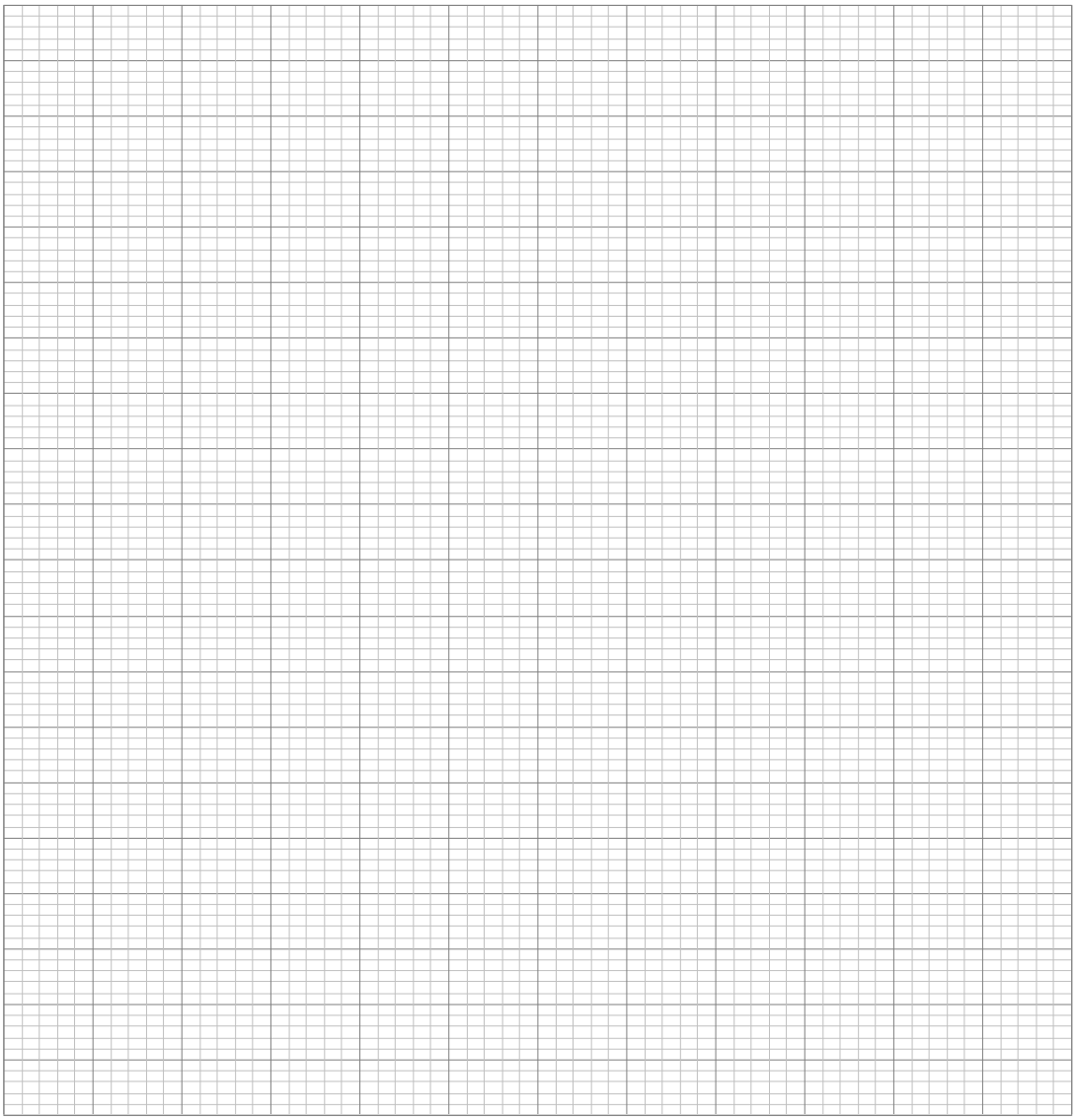
3.1. Write down the equation of the reaction which occurs during the titration:

3.2. Why is it important not to leave the bottle with the filtrate open and perform the titration directly after taking the aliquot? Support the answer with a side-reaction equation:

3.3. Calculate K_{sp} at temperatures recorded during the experiment:

T_1 = _____ K $K_{sp,1}$ = _____	T_2 = _____ K $K_{sp,2}$ = _____	T_3 = _____ K $K_{sp,3}$ = _____

3.4. Plot the graph $\ln K_{sp}$ vs $1/T$ and find ΔH^0 and ΔS^0 for the dissolution of $Ca(OH)_2$ in water:



ΔH^0 = _____ J/mol ΔS^0 = _____ J/(mol·K)