The 2nd Olympiad of Metropolises

Chemistry

Practical Problems

September 5, 2017

Moscow, Russia

General directions

- **Lab safety:** follow the general rules accepted in chemistry labs; no eating or drinking in the lab.
- **Violation of lab safety rules:** you get one warning only; offend again: you are disqualified.
- **The exam includes two tasks:** on Analytical and Organic chemistry. You can start your work with any task. 15 min for reading the set before you start to work.
- **Time:** 4 h 30 min to complete all the tasks. 30 min warning before the end.
- **When entering the lab** search for the table with your Student code.
- **Your student code:** get sure this is present on **every page.**
- **Answers:** only in the answer boxes in the booklet, nothing else will be graded. Relevant calculations have to be shown when asked for.
- **Use only the pen and calculator provided.**
- **More chemicals** needed? Ask your lab assistant. No penalty for this.
- **Questions** concerning safety, apparatus, chemicals, toilet break: **ask your lab assistant.**
- **Chemical waste** carefully pour in the sink at your working place.
- **Official English version: available** on request **for clarification only.** Ask your lab assistant.
- **After the stop signal:** put your booklet aside and leave it at your working place.
- **You must stop your work immediately after the stop signal has been given. A 5 min delay will result in zero points for the current task.**
- **During the Practical exam, some items of the glassware are expected to be used several times. Clean these carefully.**
- **Booklet with the tasks on Organic and Analytical chemistry and answer boxes: 15** pages (incl. the cover sheet and Periodic table of elements).

Reagents

Reagent	Quantity	Placed in	Labeled
Task 1			
On each workplace			
Water sample containing Fe^{2+}/ Fe^{3+} mixture	90 mL	120 mL container	Sample
Solid $K_4Fe(CN)_6 \cdot 3H_2O$	3.16 g	50 mL volumetric flask	$K_4Fe(CN)_6$
Sulfuric acid 3M	200 mL	Two 100-mL red-capped containers	H_2SO_4
$KMnO_4$ solution	50 mL	120 mL container	$KMnO_4$
Reinhardt-Zimmermann solution	40 mL	60 mL container	R-C mixture
Phenylanthranilic acid, 0.1% solution	4 mL	Dropper	Indicator
Granulated zinc	2 granules	150 mL beaker	None
On the table of common use			
Hydrochloric acid (1:1 v/v)	100 mL (to be shared by 7 students)	120 mL containers of common use	HCl (1:1)
Task 2			
On each working place			
Pinacol	15 g	Pear-shaped round bottom flask, 100 mL	None
Sulfuric acid, 25% solution	70 mL	Plastic container, 100 mL	H_2SO_4 25%
Methylene chloride	20 mL	Plastic container, 100 mL	CH_2Cl_2
Calcium chloride	2 g	Plastic container, 100 mL	$CaCl_2$

Glassware and equipment

Item	Quantity
Task 1	
On each working place	
Wash bottle with distilled water	1
Laboratory stand with burette clamp	1
25 mL beaker	1
60 mL container (without cap)	1
150 mL heat-proof beaker (with zink)	1
Watch glass	1
25 mL cylinder	1
10 mL cylinder	1
5 mL bulb (Mohr) pipette	1
10 mL pipette	1
25 mL burette	1
Plastic funnel	1
200 mL Erlenmeyer (conical flat-bottom) flask	2
50 mL volumetric flask	2
100 mL volumetric flask	1

Task 2	
On each working place	
Laboratory stand (blue)	2
Flask clamp	1
Condenser clamp	1
Ring for separation funnel	1
Hot-plate magnetic stirrer	1
Magnetic stir-barr	2
White flask support	1
Adjustable lab jack lift support	1
Wurtz adapter	2
Thermometer	1
Condenser	2
Foil (a piece)	1
Joint clips	3
Pear-shaped round-bottom flask, 100 mL (with the substance)	1
Pear-shaped round-bottom flask, 100 mL (empty)	1
Pear-shaped round-bottom flask (receiver), 50 mL (empty)	3
Pear-shaped round-bottom flask (receiver), 50 mL (with your Student code) with a stopper	1
Chemical funnel	1
Separatary funnel	1
Glass beaker, 250 mL	1
Plastic beaker, 150 mL	1
Vigreux fractionating column	1
Glass bend adapter	1
Distilling receiver cow	1
Teflon sleeve for 14/23 ground tapered joints	20
Filter paper	2
Glass ground joint stopper	4
Pasteur pipette	2
On the table of common use	
Foil	
Refractometer Refracto 30GS	
Problems 1 and 2	
On each working place	
Rubber finger protectors for handling hot items	1 pair
Pipette filler	1
On the table of common use	
Kitchen paper roll	
Filter paper	
Gloves (choose your size)	

Question	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**	**1.6**	**1.7**	**1.8**	**2.1**	**2.2**	**2.3**	**2.4**	**Total**
Points	13	13	14	1	1	1	1	1	1	1	2	1	**50**
Result													

Task 1. Titrimetric determination of free iron in a water sample (20 marks).

Control of water quality is an important issue for modern metropolises. Iron is one of the regulated components. In this task you will titrimetrically determine the total iron (II and III) content in a model river water sample. To do so, you will carry out oxidation of Fe(II) with permanganate. You will perform two determinations: one after preliminary reduction of Fe(III) with zinc to Fe(II), and another one without reduction (only Fe(II) is titrated). Beforehand, you will have to standardize the working permanganate solution.

Standardization of permanganate solution with potassium hexacyanoferrate

Dissolve the weighed amount of solid $K_4Fe(CN)_6$ in the 50 mL graduated flask in ca. 25 mL of 3 M H_2SO_4 solution. Bring up to the mark with water and mix thoroughly.

Fill the burrette with $KMnO_4$ solution (use the funnel). Note: you are provided with dry and clean burettes and pipettes. Do not spend solutions for rinsing the glassware.

Transfer with the volumetric pipette a 5.00 mL aliquot of the prepared hexacyanoferrate solution into the conical flask. Add with the cylinder 15 mL of 3 M H_2SO_4 solution and 15 mL of water. Mix the solution and titrate it with $KMnO_4$ solution. Add the titrant dropwise swirling the flask constantly. Repeat the titration until the results differ by less than 0.1 mL (the number of titrations is not graded).

1.1. Write down the volumes of permanganate solution used for hexacyanoferrate titration:

Titration number	V_{init}, mL	V_{final}, mL	V_1, mL
1			
2			
3			
Your accepted volume, mL:			

Titration of the sample solution with potassium permanganate (without prior reduction)

Pipette 5.00 mL of the standardized potassium permanganate solution into a 100 mL volumetric flask and bring it up to the mark with distilled water. Mix the solution thoroughly. Wash the burette and fill it with the prepared potassium permanganate solution.

Pipette a 10.0 mL aliquot of the sample solution into a conical titration flask, add 5 mL of the Reinhardt-Zimmermann solution, 10 mL of 3M H_2SO_4 solution, 10 mL of water, and 5 drops of the Phenylanthranilic acid solution. Titrate the prepared mixture with the $KMnO_4$ solution till light-orange coloration appears. Repeat the titration as necessary.

Note: titrate the prepared mixtures immediately. Prepare the next portion of the sample **just before the titration**.

1.2. Write down the volumes of the permanganate solution used for titration:

Titration number	V_{init}, mL	V_{final}, mL	V_2, mL
1			
2			
3			
Your accepted volume, mL:			

Titration of the sample solution with potassium permanganate with prior reduction of Fe(III)

Transfer with the 10.0 mL pipette 30.0 mL of the sample (from the 120 mL container) into the 150 mL glass beaker containing zinc granules. Add with a cylinder 10 mL of HCl (1:1 v/v). Cover the beaker with the watch glass and keep heating for 30 min. Cool the beaker under tap water down to nearly room temperature.

Transfer the solution from the beaker into the 50 mL volumetric flask (thoroughly wash the beaker containing the non-dissolved zinc granules with water). Bring the solution in the flask up to the mark and mix. Pipette a 10.0 mL aliquot of the prepared solution into the conical flask; add 5 mL of the Reinhardt-Zimmermann solution, 10 mL of 3M H_2SO_4 solution, 10 mL of water and 5 drops of the Phenilanthranilic acid solution. Swirl the flask and titrate the mixture with the potassium permanganate solution until the color changes from lemon-yellow to light-orange. Repeat the titration as necessary.

Note: titrate the prepared mixtures immediately. Prepare the next portion of the sample **just before the titration**.

1.3. Write down the volumes of the permanganate solution used for titration of the sample (with reduction of Fe(III)):

Titration number	V_{init}, mL	V_{final}, mL	V_3, mL
1			
2			
3			
Your accepted volume, mL:			

1.4. Calculate the concentration of $K_4Fe(CN)_6$ solution in mol/L (mass of the trihydrate is 3.16 g).

c =

1.5. Write down the ionic reaction equation occurring upon standardization of the permanganate solution:

1.6. Calculate the concentrations of non-diluted and diluted potassium permanganate (mol/L) based on the titration results:

c (initial) =

c (diluted) =

1.7. Write down two reactions occurring upon heating of the acidic sample solution with zinc:

1.

2.

1.8. Calculate the concentration of iron(II) and iron(III) (mg/L) in the sample based on the titration results:

Calculations:

Concentration of iron(II) _____ mg/L

Concentration of iron(III) _____ mg/L

2. Answer the theoretical questions.

2.1. Natural water often contains a considerable amount of chloride ions. Write down the competing reaction equation that interferes with the titrimetric determination of Fe(II) with permanganate in the presence of chloride:

2.2. Free chlorine can be obtained by the reaction of manganese dioxide with hydrochloric acid. Write down the balanced equation of this reaction:

2.3. Permanganate reacts extremely slowly with diluted hydrochloric acid solutions in the absence of iron. However, the reaction accelerates upon addition of a Fe(II) salt, and the characteristic chlorine odor appears. Suggest a scheme of reactions explaining the catalytic action of Fe(II) in the system (use the properties of manganese compounds you have written in i. **2.2**):

No catalyst:

In the presence of Fe(II):

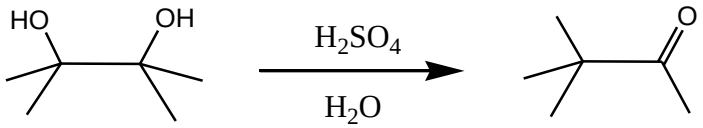
2.4. To get rid of the interfering effect of chloride ions (i. **2.1**) you have added the Reinhardt-Zimmermann solution containing Mn(II) ions to the titrated solution (the manganese action is due to decreasing the redox potential of MnO_4^-/Mn^{2+}). Addition of fluoride ions is an alternative method to avoid the interfering action of chloride ions on the titration process. Write down the reaction equation explaining a possible mechanism of the protecting action of fluoride (take into account your scheme in i. **2.3**):

Question	**1.1**	**2.1**	**2.2**	**2.3**	**2.4**	**Total**
Points	40	4	2	3	1	**50**
Result						

Task 2. Pinacol–pinacolone rearrangement (20 marks).

Various skeletal rearrangements are used up-to-date in fine organic synthesis, pinacol-pinacolone rearrangement being among the most popular ones due to numerous benefits when applied for preparation of highly efficient drugs.

Pinacol-pinacolone rearrangement was mentioned for the first time in 1859-1860, when W.R. Fittig reported about acetone interaction with potassium followed by the pre-product reaction with sulfuric acid. Still, he failed to identify the products properly, since rearrangements were unknown by that time. Only 1873, A.M. Butlerov postulated the mechanism and determined the reaction products based on his theory of chemical structure. Thus, this rearrangement was the first one the chemists faced with ever. In this task, you are expected to carry out the classical variant of the reaction:



Pinacole Pinacolone

<u>Pinacolone synthesis</u>

Set up the apparatus as shown in fig. 1. <u>All joints must be supplied with Teflon sleeves.</u> Place the magnetic stir-bar (2) in the pear-shaped round bottom flask (1) containing 15 g of pinacol. Fix the flask (1) in the stand clamp (3) at 1-2 mm over the magnetic stirrer plate (important: the flask bottom part must not touch the plate). Pour 70 mL of 25 % sulfuric acid solution into the flask (1) through the chemical funnel. Rinse the funnel with water in the sink and take aside. Attach the Wurtz adapter (4) to the flask, insert the thermometer (5) in the adapter. Equip the descending condenser (6) with water hoses, attach the lower hose to the water tap, and put the upper hose in the sink. Attach the glass bend adapter (7) to the condenser; fix the joint with clips. Fasten the condenser in the stand clamp (8), attach it to the Wurtz adapter (4), and fix the joint with clips. Attach the 50 mL pear-shaped receiver flask (9) to the glass bend adapter (7), fix the joint with clips. Put the white support (10) under the flask (9). Turn the tap to provide for slow water flow in the condenser. Wrap the flask (1) and Wurtz adapter (4) with 3-4 layers of foil up to the condenser ground tapered joint, leaving a small hole to look after the reaction mixture. Switch on stirring at «2» and heating at «6». Wait until the thermometer readings are within the

95-102 C range, and then continue heating for approximately another 20 min. While heating, you are expected to carry out the other task or complete the theoretical parts.

Note. If you experience difficulties in reading the thermometer, seek for help from your lab assistant.

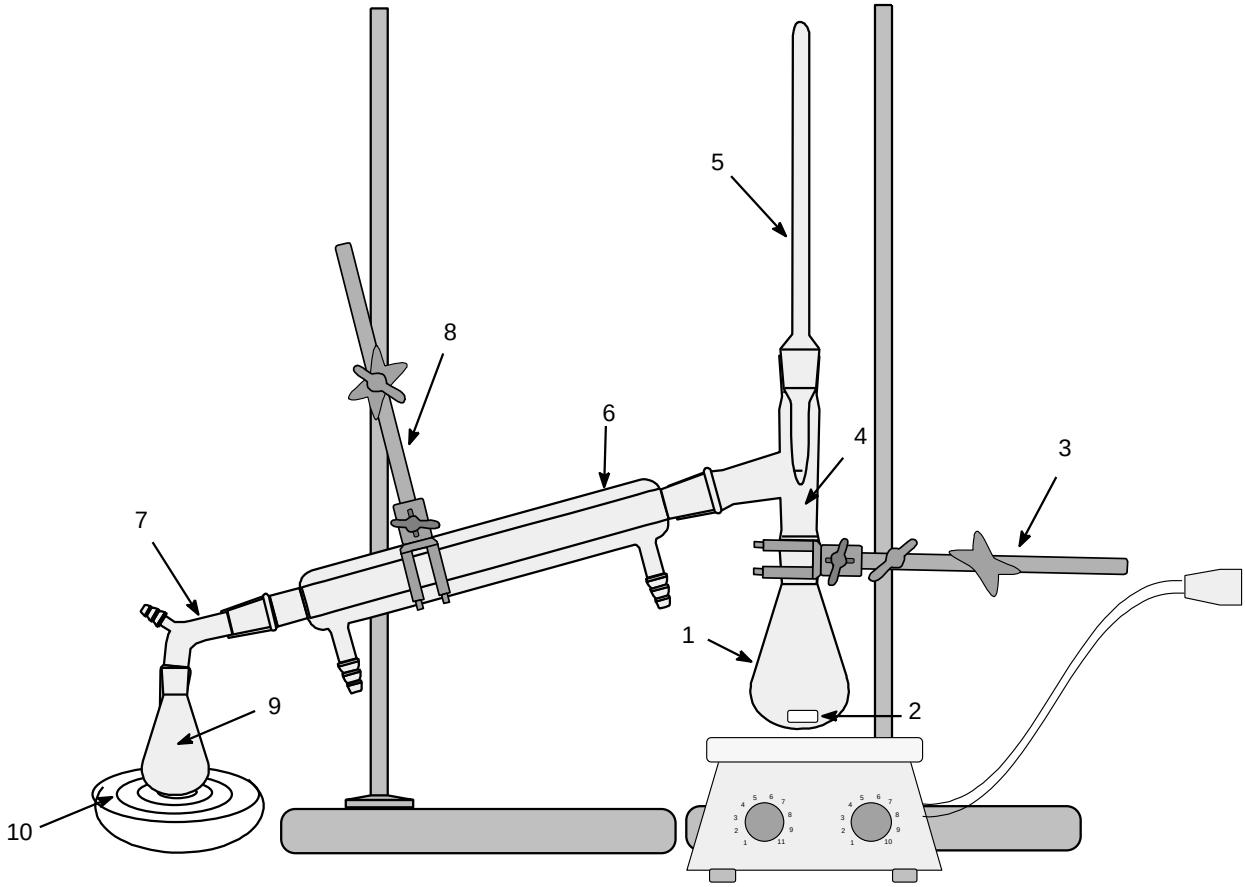


Fig. 1. The synthesis setup.

Switch off heating and stirring. Use the rubber finger protectors (take care: hot!) to remove the foil. Take the magnetic stirrer aside. In 3-5 min., disconnect the receiver flask (9) containing a two-phase liquid and stopper the flask. Turn off the tap, disconnect the hose from the tap, pour water out of the condenser (6) and separate the hoses. Disconnect the condenser (6) and glass bend adapter (7) and deliver these to your lab assistant.

Separation of the reaction system

On the stand, change the clamp (8) by the ring (11) (fig. 2), and place the separatory funnel (12) into it. Make sure that the funnel valve is closed. Place the glass beaker (13) under the funnel (12). Transfer the two-phase liquid from the receiver (9) into the separatory funnel (12) using the chemical

funnel (14), then wipe the chemical funnel (14) dry with napkin. Pour out the lower aqueous phase into the beaker (13), and the upper organic phase into the plastic container labeled $CaCl_2$ (15). Stopper the container, gently mix the contents, and put aside for 10-15 min. Deliver the separatory funnel (12) to your lab assistant. Wipe the thermometer (5) with a napkin and put aside.

Using the rubber finger protectors (take care: hot!) disconnect the Wurtz adapter (4) from the flask (1). Delver the Wurtz adapter (4) and the flask (1) to your lab assistant.

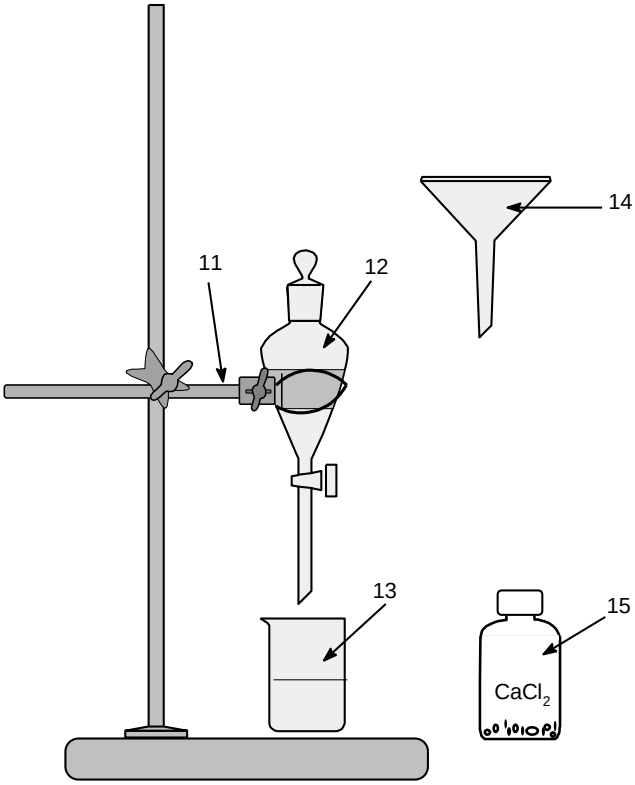


Fig. 2. Setup for phase separation.

Weigh the 150 mL plastic beaker (16) containing the empty 50 mL receiver flask (17) labeled with your Student code and the labeled stopper. Write down the mass value into Table 1.

Purification of the product

Set up the apparatus as shown in fig. 3. All joints must be supplied with Teflon sleeves. Attach the weighed receiver flask (17) to the distilling receiver cow (20), fix the joint with clips. Bring the magnetic stirrer to the former place under the clamp (3). Place the clean magnetic stir-bar into the clean 100 mL pear-shaped round bottom flask (18), fix the flask in the stand clamp (3) over the magnetic stirrer platform. Insert the funnel (14) into the flask; equip the funnel with the paper filter. Port out the contents of the 100 mL container (15) into the funnel. Add ca. 10 mL of CH_2Cl_2 into the container (15) with the residual amount of $CaCl_2$. Stopper the container, gently mix and then also transfer the contents into the funnel (14). Deliver the funnel (14) with the paper filter to your lab assistant.

Attach the Vigreux fractionating column (19) and the clean Wurtz adapter (4) to the flask (18), and connect the thermometer (5) to the Wurtz adapter (4). Change the ring (11) by the clamp (8). Equip the clean condenser (6) with water hoses, attach the lower hose to the water tap, and put the upper hose in the sink. Fasten the condenser in the stand clamp (8), attach it to the Wurtz adapter (4), and fix the joint with clips. Attach the distilling receiver cow (20) with three receiver flasks to the lower ground tapered joint of the condenser. Fix the distilling receiver cow joint with clips. Rotate the distilling

receiver cow so that the receiver flask with your Student code (17) is positioned upwards. Adjust the lab jack lift support (21) so that it supports the receiver flasks in the proper position. If needed, you can use the white support (10). Turn the tap to provide for slow water flow in the condenser.

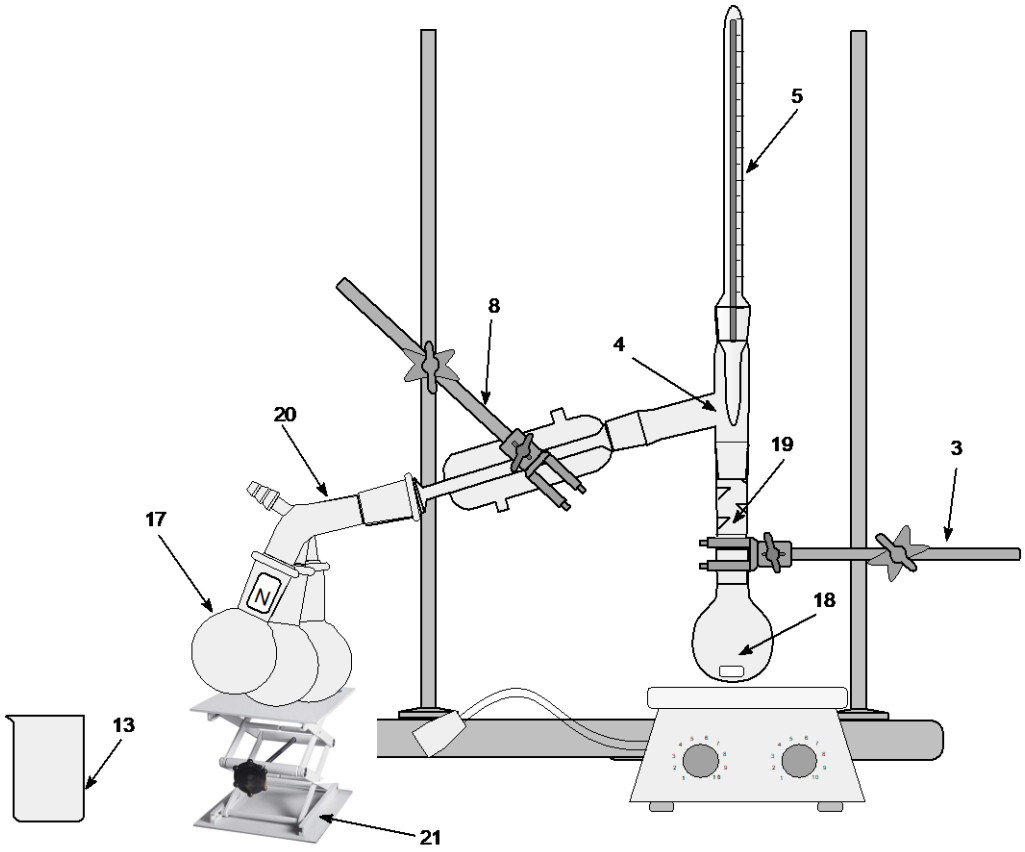


Fig. 3. Setup for distillation.

Tightly wrap the Vigreux fractionating column (19), Wurtz adapter (4) up to the condenser ground tapered joint and the flask with the mixture (18) with 2-4 layers of foil, leaving a small hole to look after the reaction mixture. Switch on stirring at «2» and heating at «4». Distill methylene chloride (boiling temp. of 42 ºC) into an unlabeled receiver flask. Switch over the heating to «6» when the temperature raise up to 60 ºC. Distil the residue into the receiver flask with your Student code, collecting the fraction within 97-107 ºC range. Once only ca. 1 mL of the substance is left in the flask (18), turn off heating and stirring and use the rubber finger protectors (take care: hot!) to remove the foil. Take the magnetic stirrer aside.

Disconnect the receiver flask with your Student code (17) form the distillation receiver cow, remove the Teflon sleeve, and apply the labeled stopper to the receiver flask. Weigh the latter in the 150 mL plastic beaker (16). Calculate the mass and yield of the product. Measure its refractive index by using the Refractometer (see the directions below).

1.1. Write down the results in Table 1.

Leave the closed receiver flask with the product in the beaker on your working place.

Table 1. Results record.

Mass of the empty flask (17) with the stopper (in the beaker), g	Mass of the flask (17) with the product and stopper (in the beaker), g	Mass of the product, g	Yield, %	Refractive index n_D

Directions on using Refractometer REFRACTO 30GS

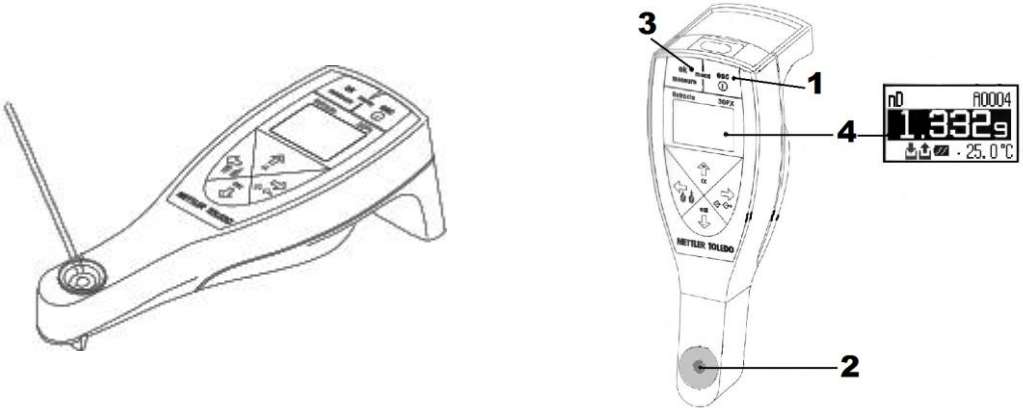


Fig. 4. Using the Refracto 30GS

1. To switch Refracto 30GS on, press and hold “ESC” button (1) until the display appears. The instrument is ready for operation. It switches off automatically if not operated for 10 min.
2. Clean the cell (2) with a napkin wetted with the solvent from the washing bottle labeled “cleaning solvent”. Dry the cell with another napkin.
3. Make sure the sample to be measured has reached ambient temperature and is homogeneous.
4. Apply 10 drops of the sample onto the measuring cell (2) using the Pasteur pipette.
5. To start the measurement press and hold the ok button (3) until the beep.
6. Take the value of the refraction index from the display (4) and write it down in Table 1.
7. Collect the sample from the cell (2) using the Pasteur pipette and put it back into your flask.
8. Clean up the cell with a napkin wetted with the solvent from the washing bottle labeled “cleaning solvent”. Dry the cell with another napkin.

2. Answer the theoretical questions.

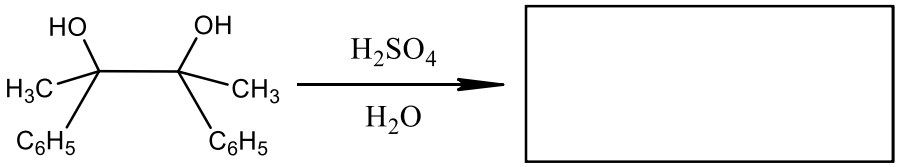
2.1. Write down the mechanism of the pinacol-pinacolone rearrangement:

2.2. What is the role of sulfuric acid in the process? Tick the correct answer(s).

- ☐ An electrophile
- ☐ A Lewis base
- ☐ A proton donor
- ☐ A catalyst of interphase transfer
- ☐ A sulfating agent
- ☐ An oxidizer

2.3. Complete the scheme of pinacol preparation. Draw the missing substances and balance the scheme with coefficients.

2.4. What is the product of the hereunder reaction? Draw its structure.



IUPAC Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen [1.007; 1.009]																	2 **He** helium 4.003
3 **Li** lithium [6.938; 6.997]	4 **Be** beryllium 9.012											5 **B** boron [10.80; 10.83]	6 **C** carbon [12.00; 12.02]	7 **N** nitrogen [14.00; 14.01]	8 **O** oxygen [15.99; 16.00]	9 **F** fluorine 19.00	10 **Ne** neon 20.18
11 **Na** sodium 22.99	12 **Mg** magnesium 24.31											13 **Al** aluminium 26.98	14 **Si** silicon [28.08; 28.09]	15 **P** phosphorus 30.97	16 **S** sulfur [32.05; 32.08]	17 **Cl** chlorine [35.44; 35.46]	18 **Ar** argon 39.95
19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.87	23 **V** vanadium 50.94	24 **Cr** chromium 52.00	25 **Mn** manganese 54.94	26 **Fe** iron 55.85	27 **Co** cobalt 58.93	28 **Ni** nickel 58.69	29 **Cu** copper 63.55	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.72	32 **Ge** germanium 72.63	33 **As** arsenic 74.92	34 **Se** selenium 78.96(3)	35 **Br** bromine 79.90	36 **Kr** krypton 83.80
37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zirconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.96(2)	43 **Tc** technetium	44 **Ru** ruthenium 101.1	45 **Rh** rhodium 102.9	46 **Pd** palladium 106.4	47 **Ag** silver 107.9	48 **Cd** cadmium 112.4	49 **In** indium 114.8	50 **Sn** tin 118.7	51 **Sb** antimony 121.8	52 **Te** tellurium 127.6	53 **I** iodine 126.9	54 **Xe** xenon 131.3
55 **Cs** caesium 132.9	56 **Ba** barium 137.3	57-71 lanthanoids	72 **Hf** hafnium 178.5	73 **Ta** tantalum 180.9	74 **W** tungsten 183.8	75 **Re** rhenium 186.2	76 **Os** osmium 190.2	77 **Ir** iridium 192.2	78 **Pt** platinum 195.1	79 **Au** gold 197.0	80 **Hg** mercury 200.6	81 **Tl** thallium [204.3; 204.4]	82 **Pb** lead 207.2	83 **Bi** bismuth 209.0	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium		114 **Fl** flerovium		116 **Lv** livermorium		

57 **La** lanthanum 138.9	58 **Ce** cerium 140.1	59 **Pr** praseodymium 140.9	60 **Nd** neodymium 144.2	61 **Pm** promethium	62 **Sm** samarium 150.4	63 **Eu** europium 152.0	64 **Gd** gadolinium 157.3	65 **Tb** terbium 158.9	66 **Dy** dysprosium 162.5	67 **Ho** holmium 164.9	68 **Er** erbium 167.3	69 **Tm** thulium 168.9	70 **Yb** ytterbium 173.1	71 **Lu** lutetium 175.0
89 **Ac** actinium	90 **Th** thorium 232.0	91 **Pa** protactinium 231.0	92 **U** uranium 238.0	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

Key: atomic number **Symbol** name standard atomic weight

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Notes

- IUPAC 2009 Standard atomic weights abridged to four significant digits (Table 4 published in *Pure Appl. Chem.* 83, 359-396 (2011); doi:10.1351/PAC-REP-10-09-14). The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements which lack isotopes with a characteristic isotopic abundance in natural terrestrial samples. See PAC for more details.

- "Aluminum" and "cesium" are commonly used alternative spellings for "aluminium" and "caesium."

- Claims for the discovery of all the remaining elements in the last row of the Table, namely elements with atomic numbers 113, 115, 117 and 118, and for which no assignments have yet been made, are being considered by a IUPAC and IUPAP Joint Working Party.

For updates to this table, see iupac.org/reports/periodic_table/. This version is dated 1 June 2012.