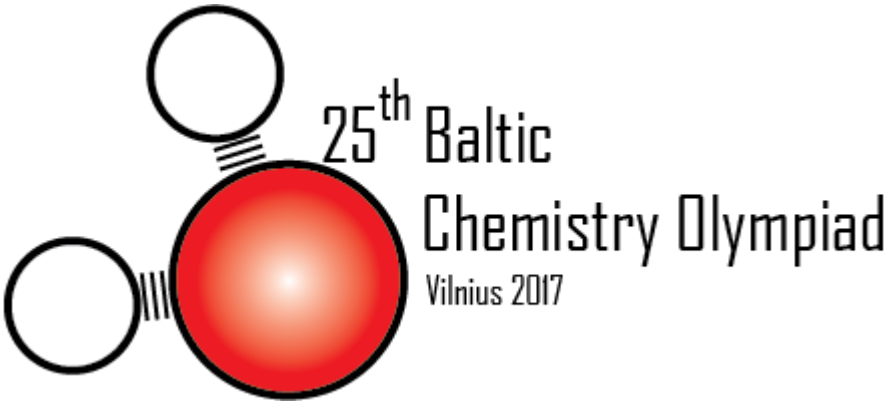


Practical Exam

April 29, 2017
Vilnius, Lithuania

	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**

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

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 = 1.66053904×10^{-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 $[\mathrm{A}] = [\mathrm{A}]_0 - kt$ $\qquad$ First order $\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$

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

Arrhenius equation

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

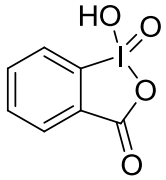
General Directions

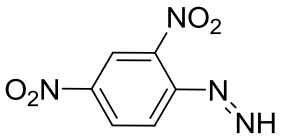
- Follow safety rules. No eating or drinking in the lab. Always wear your lab coat and safety goggles when being in the lab. Ask your lab assistant for the gloves
- Write your name and student code on each page of the answer sheets.
- We suggest to start from the first task.
- During the Practical exam, 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.
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers (numbers and units) only when your work is shown.
- You must **stop** working when the **STOP** command is given.
- Do not leave your seat until permitted by the supervisors.
- More chemicals or glassware needed? Ask your lab assistant. Replacement of each item will be penalized with 1 point of 40 for the Practical examination.
- The official English version of this examination is available on request only for clarification.

Practical task #1
Oxidize and identify!

20 points

Oxidation is a very common and useful reaction in organic chemistry allowing to convert one functional group to another, for example: primary alcohols can be converted to aldehydes and carboxylic acids, secondary alcohols to ketones, alkenes to epoxides, diols etc. The oxidized compounds can be further used in another reactions. A great variety of different oxidizing agents, having different properties, are being used, such as ozone, chromates, dichromates, $KMnO_4$, peracids, peroxides etc. In this task, you will have to oxidize unknown alcohol to a ketone using quite mild and modern oxidizing agent IBX (2-Iodoxybenzoic acid). Then you will let react a small amount of your synthesized ketone with DNPH (2,4-Dinitrophenylhydrazine) resulting in a corresponding hydrazone. Nearly all hydrazones are coloured compounds which can be identified chromatographically by TLC (thin layer chromatography). You will not need a UV lamp because coloured hydrazones can be seen without it on a TLC plate. The main aim of your work is to identify the structure of an alcohol which is given to you.

IBX 

DNPH 

Chemicals at your workplace:
Unknown alcohol (320 mg in a 25 ml Erlenmeyer flask)
4 solutions of known hydrazones (in 4 corked test tubes)
DNPH solution (labeled DNPH, 1 ml in a small glass bottle)

Chemicals for general use:
2-Iodoxybenzoic acid (labeled **IBX**, at the balance)
Dimethyl Sulfoxide (labeled **DMSO**, in a fume hood)
Chloroform (labeled **CHLOROFORM**, in a fume hood)
Isopropanol (labeled **ISOPROPANOL**, on the upper shelf, near your workplace)
Toluen (labeled **TOLUEN**, in a fume hood)
$CaCl_2$ (labeled $CaCl_2$, at the balance)
Saturated $NaHCO_3$ solution (labeled $NaHCO_3$, in a fume hood)

Labware and equipment:
1 25 ml Erlenmeyer flask (with an unknown alcohol inside)
1 Watch glass
1 Hot-plate magnetic stirrer
1 Stirring bar
1 Laboratory stand with a clamp
1 Separatory funnel with a cork
1 Spatula
1 Glass rod
5 Test tubes (4 of them with corks)
1 Test tube rack
1 Distilled water bottle (for both practical tasks)

1 Glass funnel with a filter paper
1 Waste bottle
1 Pair of gloves (for both practical tasks)
1 Safety goggles (for both practical tasks)
1 Ruler (for both practical tasks)
2 Weighing boats
1 Pre-weighed 50 ml beaker (labeled **PRODUCT**)
2 100 ml beakers for extraction
1 25 ml beaker for hydrazone synthesis
1 TLC set: covered beaker, silica gel plate, glass capillaries (2 pcs. in a test tube), tweezers
1 Vacuum filtration equipment: Bunsen flask, Buchner funnel, filter paper
1 Water bath
1 Thermometer
1 10 ml graduated cylinder (for both practical tasks)

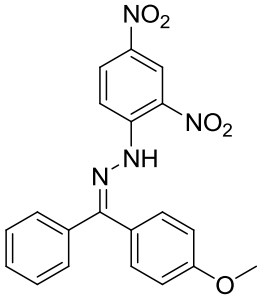
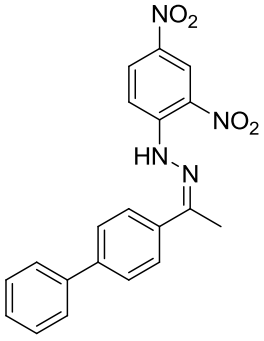
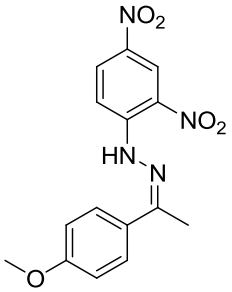
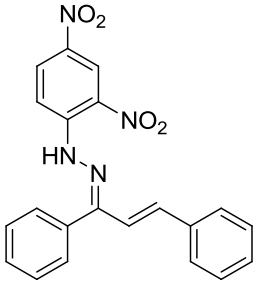
Balances, vacuum aspirators, hot-plates in the fume hoods and cotton gloves are for general use.
Wearing safety goggles is compulsory!
DMSO penetrates skin very well, so is it highly recommended to wear gloves when having contact with DMSO.
If you need you can get one extra TLC plate, 2 extra glass capillaries and as many gloves as you need without a punishment.
IBX is a potentially explosive compound when heated above 200 °C. Work with it very carefully.

PROCEDURES:

1. Put water bath onto a hot-plate magnetic stirrer and heat it until it starts intensively evaporating (approx. 80-90 °C).
2. While a water bath is being heated, weigh 600 mg of IBX and add it to 25 ml Erlenmeyer flask containing unknown alcohol. Pour 3 ml of DMSO into the same flask, swirl the flask and insert the stirring bar.
3. Clamp this flask on the laboratory stand and immerse it into hot water. Start stirring the mixture. Cover the flask with a watch glass. Now leave the reaction mixture for 45 minutes. Heat and stir it all the time. Refill the water bath with water when needed. You can perform second practical task while the reaction occurs.
4. After 45 minutes pull out the flask from the water bath and cool it to room temperature. For faster cooling you can change the hot water in the water bath with cold tap water and cool the reaction mixture into it. Do not break the glass due to thermo-shock! (When changing hot water to cold water, let the water bath's glass to cool down before pouring cold water into it!)
5. After cooling pour 10 ml of chloroform into Erlenmeyer flask and mix everything very well. Then clamp separatory funnel on the laboratory stand, put a glass funnel directly into separatory funnel and using filter paper filter the reaction mixture (the stirring bar also goes on the filter paper). The filtrate collects in a separatory funnel. Then pour another 5 ml of chloroform in the Erlenmeyer flask and pour everything in a glass funnel again. Do the same procedure the third time. Now you have 20 ml of chloroform solution in a separatory funnel. Take the glass funnel out and put it aside.
6. Pour 10 ml of saturated $NaHCO_3$ solution into a separatory funnel and also add approx. 5 ml of distilled water. Take a separatory funnel out of the laboratory stand, shake everything very well and then clamp the separatory funnel back on the laboratory stand and leave it still for one minute. Separate organic-phase from water-phase. Use two 100 ml beakers for that. Pour water-phase into WASTE container and

organic-phase back into separatory funnel. (If some insoluble materials are seen in the phase border, discard them.) Repeat the procedure nr. 6 one more time.

7. Then add approx. 15 ml of distilled water in a separatory funnel and again do the same: shake everything very well, leave it calm for one minute and separate two phases. Discard water-phase, pour organic-phase back into separatory funnel. And then repeat the procedure nr. 7 one more time.
8. After that, collect your organic phase in a beaker. Organic phase might be cloudy because of small amount of water inside it. So, weigh approx. 2 g of $CaCl_2$ and add it into a beaker with organic-phase. Swirl the mixture for several minutes until the solution becomes clear. Then very gently decant the liquid into a **PRODUCT** beaker. Make sure that no solid material is in **PRODUCT** beaker. Ask your lab assistant for help to evaporate the solvent in a fume hood. After evaporating the solvent leave the beaker to cool down for 5 minutes.
9. Weigh the PRODUCT beaker. Show the mass to the lab assistant and get his signature.
10. Then weigh approx. 40 mg of your synthesized ketone, put it into a 25 ml beaker, pour 3 ml of isopropanol and heat it gently until the solid dissolves. Then pour 1 ml of DNPH solution. Leave the mixture for several minutes. Filter the hydrazone using vacuum filtration equipment. Wash the precipitate with isopropanol.
11. Dissolve a few milligrams of the hydrazone in an empty test tube (use chloroform as a solvent).
12. Perform TLC analysis. One of the four known hydrazones that you are given is the same as you have just synthesized. On the same TLC plate using glass capillaries place small amounts of these 4 known hydrazones solutions that are given to you and also a small amount of the hydrazone solution you have just synthesized. Place these solutions on the dots marked with pencil. After that, the coloured dots you have just made should be clearly visible. If they are not, repeat the procedure again until they become visible. Then pour about 2 ml of toluene in a TLC covered beaker. Place your TLC plate into that beaker so that the coloured dots would be at the bottom. Let the solvent rise till the finish line marked on the TLC plate. Then take the TLC plate out and evaluate your results. Choose and decide which hydrazone you have and consequently which alcohol you had been given.
13. Calculate Rf values. Rf value is a path length that a hydrazone travelled divided by the path length that a solvent travelled. Show your TLC plate to a lab assistance and get his signature that you leave a TLC plate at your workplace in a zip plastic bag.

Test tube number	1	2	3	4
Structure of a hydrazone inside a test tube				

Fill in the answer sheets thoroughly.

Practical task #2
Determination of reaction rate law

20 points

Determination of reaction rate law sometimes can be a difficult task, since you have to track concentrations of several reacting species simultaneously. Due to this difficulty determination is often carried out when all but one reacting species are in a large excess, hence their concentrations effectively don't change. This simplifies the analysis, however you have to carry out the experiment for each substance that takes place in the reaction separately. In this work you will determine reaction rate law only for one of reacting species.

Substances:

0.500 M $Na_2S_2O_3$ solution	1 M KI solution
1 M H_2SO_4 solution	Starch solution
H_2O_2 solution	

Equipment:

1	25-mL burette
1	250-300mL Erlenmeyer flask
1	100-mL volumetric flask
1	10-mL volumetric pipette
1	10 mL graduated pipette
1	Plastic Pasteur pipette
1	100-mL and 10-mL graduated cylinders
1	Pipette bulb
1	Funnel
1	Lab stand and clamp
1	Chronometer
1	Wash bottle with distilled water
1	Waste container
1	Ruler, pencil, eraser

How to use the stopwatch:

- press „mode" button once and you will be in the chronograph mode
- press „reset" button once to start from zero
- press „ST./STP." button once to start
- press „ST./STP." button once more to stop
- press „reset" button to start from zero again

THEORY

In this assignment, you are to study the following reaction:

$$H_2O_{2\,(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2\,(aq)} \quad \text{(Slow)} \qquad (1)$$

Under the conditions of the experiment, the iodide and hydrogen ions are present in large excess. Consequently, their concentrations remain effectively constant during the reaction and do not appear on the right-hand side of the rate law (they are included in the rate constant). The rate law will thus depend only upon the concentration of hydrogen peroxide:

$$-\frac{d[H_2O_2]}{dt} = k[H_2O_2]^n \qquad (2)$$

We will determine the order ***n*** and the value and units of the rate constant ***k***. Although some reactions have quite complicated rate laws with fractional orders, we will test only for the relatively simple cases of n = 0, 1, or 2. In order to do this, it is necessary to integrate the rate law. The exact form of the integrated rate law depends upon the value of n. When n = 0 (zero order), the integrated rate law is as follows:

$$[H_2O_2] = [H_2O_2]_0 - kt \qquad (3)$$

When n = 1 (first order), the integrated rate law is as follows:

$$ln[H_2O_2] = ln[H_2O_2]_0 - kt \qquad (4)$$

When n = 2 (second order), the integrated rate law is as follows:

$$\frac{1}{[H_2O_2]} = \frac{1}{[H_2O_2]_0} - kt \qquad (5)$$

Only one of the three equations (3-5) will actually fit the concentration data for the reaction (i.e., only one of the three possible orders can be correct). If one can measure the concentration of hydrogen peroxide remaining at various times during the reaction, the data may be plotted in the form of each of the three integrated rate laws; only one graph will actually be a straight line, thus indicating the correct order. The value of the rate constant k can be found from the slope of the graph.

Since it is not possible to directly analyse for the hydrogen peroxide concentration while the reaction is taking place, we will instead analyse for the amount of iodine formed and use the stoichiometric relationships to determine how much hydrogen peroxide remains. After initiating the reaction, aliquots of standard sodium thiosulfate solution are added to the reaction mixture at intervals. The thiosulfate ion reacts with the iodine formed by the principal reaction as follows:

$$I_{2\,(aq)} + 2S_2O^{2-}_{3\,(aq)} \rightarrow 2I^-_{(aq)} + 2S_4O^{2-}_{6\,(aq)} \quad \text{(Fast)} \qquad (6)$$

Since this reaction is much faster than the (1) reaction, any iodine formed by reaction (1) is immediately consumed by the thiosulfate ion. In addition, starch is added to the mixture to indicate the presence of molecular iodine:

$$I_{2\,(aq)} + I^-_{(aq)} \rightarrow I^-_{3\,(aq)} \quad \text{(Fast)} \qquad (7)$$

$$I^-_{3\,(aq)} + \text{starch} \rightarrow \text{blue complex} \quad \text{(Fast)} \qquad (8)$$

The method of analysis is as follows. The principal reaction (equation 3) is initiated in the presence of a starch solution and a timer is started. The mixture immediately turns blue as iodine is formed (see the rising line beginning at zero time in Figure 1; the rising lines indicate the formation of I_2, and the vertical lines indicate the consumption of I_2 by thiosulfate). An aliquot of standard sodium thiosulfate solution is quickly added from a burette (first vertical part of the trace on the graph). This amount of thiosulfate is deliberately in excess and will immediately consume all of the iodine formed by the principal reaction; the mixture thus becomes colorless. There is now an excess of thiosulfate ion present in the flask. As more and more iodine is produced (second rising portion of the graph), the fixed amount of thiosulfate is eventually consumed. At this point, the blue color reappears and the time is noted. This step is repeated as long as you have enough data to plot the graph.

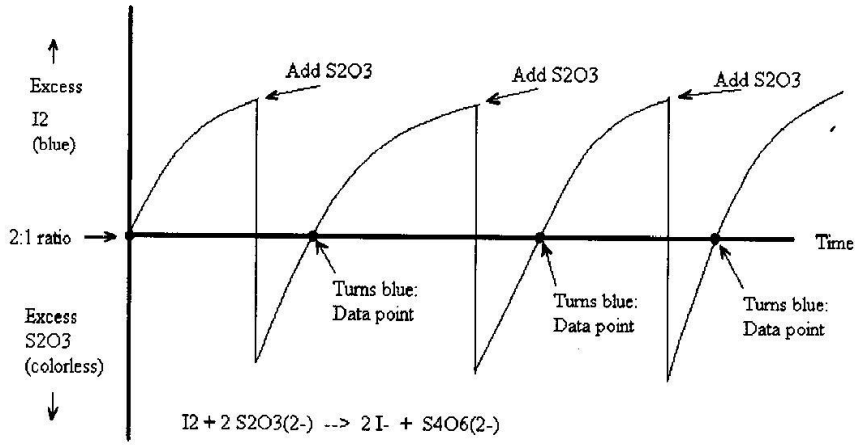


Figure 1. Relative Amounts of I_2 and $S_2O_3^{2-}$ During the Experiment

The **total** amount (in millimoles) of iodine **produced** at time **t** can then be calculated from the **total** amount of thiosulfate used up to that point (the total amount added **prior** to the color change, since the beginning of the reaction). The **total** number of moles of iodine produced is then used to calculate the **total** number of moles of hydrogen peroxide **consumed** up to that time (see stoichiometry of equation 3); this number is then subtracted from the initial number of moles of hydrogen peroxide, since the number of moles of hydrogen peroxide **remaining** is needed. Another excess of thiosulfate is added (second vertical portion of the graph) and the time is again noted when the blue color reappears (second rising portion of the graph); this process is repeated several times to obtain sets of concentration-time data for fitting to the three assumed rate laws. The initial amount of hydrogen peroxide is determined by allowing the reaction to proceed to completion and determining the total amount of iodine produced, then relating this to the total amount of hydrogen peroxide which was initially present.

Experimental Procedure

1. Prepare the thiosulfate solution of precise concentration by taking 10 mL of 0,500 M $Na_2S_2O_3$ with volumetric pipette and then pipetting it in the 100 mL volumetric flask. Dilute the solution to the mark.
2. Fill up the burette with the thiosulfate solution of precise concentration.
3. In a clean, dry Erlenmeyer flask pour 75 mL of distilled water (use a graduated cylinder), 5 mL of 1.0 **M** sulfuric acid solution (use a graduated pipette), and 2.5 mL of starch solution (use a Pasteur pipette).
4. With a volumetric pipette, pipet in exactly 10.00 mL of hydrogen peroxide solution to the same flask and mix well.
5. Quickly add 10.0 mL of 1.00 **M** potassium iodide solution from a graduated cylinder as quickly as possible, starting the timer **at the same time as the addition**. The timer must run continuously throughout the experiment. Immediately add about 1,5 mL of sodium thiosulfate solution from the burette and record the burette reading. Mix well, the blue color will disappear. When the solution turns blue again, record the timer reading **while the timer continues to run** and then add another increment of sodium thiosulfate and again record the volume and the time at which the color reappears. Continue to repeat this process until ten data points have been recorded.
6. Stop the timer and let the mixture stand for one hour. This will be sufficient time for the reaction to reach completion (in the meantime, continue doing organic chemistry practical task). **Carefully** titrate the solution with the remaining sodium thiosulfate in your burette until the blue color just disappears (it should not return). Record the final burette reading, and then clean up all of your equipment.