Practical Problems

Safety Regulations

The following regulations apply to all laboratories used for the Olympiad. Participating students must be well acquainted with these regulations and should study them seriously. These rules will be strictly followed in the 33rd IChO practical examination. Students who break any of these rules will be given only one warning before they are disqualified from the practical examination.

If any questions arise concerning safety procedures during the practical examination, students should not hesitate to ask the nearest instructor for directions.

All students are required to sign a statement agreeing that they have read and understood the rules prior to the examination.

Rules for personal safety

a. For eye protection, safety goggles must be worn in the laboratories at all times. If the student wears contact lenses, full protection goggles, which provide total seal around eyes, must be worn. All students are requested to bring their safety goggles, but we shall have some in reserve.

b. A long sleeved, knee length laboratory coat is recommended. Long pants and closed-toed shoes must be worn for individual safety. Loose clothing, open style shoes and sandals are prohibited. Long hair must be contained. Each student will have to get her/his own necessary items for herself/himself.

c. Prior to the examination, the demonstrator-in-charge will check all protective equipments to ensure that they are in order.

d. Pipetting by mouth is strictly forbidden.

e. Eating, drinking or smoking in the laboratory is strictly prohibited.

Accidents and first aid

In any chemistry laboratory, accidents can take place due to spillage of chemicals, broken glasswares and fire. Any injury, illness, or incident, however minor, must be reported to the instructor immediately so that proper corrective action can be taken up.

a. Chemicals: Every chemical in the laboratory must be handled with utmost care. Chemicals can be corrosive, flammable or poisonous. Each student should read the safety notes related to the chemicals given in the task before handling them. The following general precautions must be always followed in the laboratory :

- Chemicals should never be tasted. Use pipette bulbs or pipette fillers all the time.
- Spillage on the skin: For any spillage of chemicals, the first step is to flush the skin under cold tap water for 10 to 15 minutes and then seek first aid/or medical help as appropriate. Organic materials tend to get absorbed on the skin, so wash the skin with warm water and soap, after cleaning it with cold water. Contaminated clothing should be removed at the earliest.
- Chemicals in the eye: The proper use of safety goggles will reduce the risk of any eye injury. Even so, if there is any splash of chemicals into the eyes, wash your eyes with cold water for 15 minutes and then look for appropriate medical attention.

b. Fire: Many chemicals are flammable, and hence no open flames are permitted when such chemicals are in use. You should get familiar with the location of the nearest fire extinguisher and fire blanket.

c. Glassware: Glass is a very hard but brittle material, and can break under stress or strain. Please handle the glasswares very carefully. If breakage occurs it is essential that any particles or splinters, specially from the wounds, are removed at the earliest. The injuries must be inspected by the demonstrator-in-charge.

Please report and clean up any breakage of the glassware. Necessary replacements can be obtained from the instructor.

d. Waste Materials: Do not dispose of chemicals in the sink. Please follow all disposal rules provided in the task notes. Waste collection containers will be provided wherever necessary.

e. Care of Benches and Apparatus: Each student is responsible for her/his section of the bench. Any spillage of chemicals or water must be wiped immediately. Concentrated acid spills must be first neutralized with sodium bicarbonate and then washed with plenty of water. Your working area must be kept clean at all times. Chemicals spilled on the ground must be washed and broken glassware must be swept off immediately. Mops, brooms, dust-pans etc will be available from the preparation room.

Some important information regarding the 33rd IChO practical examination

- Time duration for the practical examination would be four and a half hours instead of five hours.
- The examination may consist of three **independent** experimental tasks. The time duration for each task may vary from one to one and a half hour.
- The examination will be conducted in two batches. Students No.1 and 2 from each team will be part of the first batch; students No.3 and 4 will be part of the second batch.
- Students of both batches will get a new set of apparatus for the examination.
- The apparatus for the examination will include both plasticware and glassware.
- The examination will not involve use of microscale apparatus.

Problem 25 Determination of aspirin in the given sample

Acetyl salicylic acid ($CH_3COO.C_6H_4.COOH$) undergoes hydrolysis when boiled gently with aqueous NaOH, which forms a basis for its estimation.

Chemicals and solutions

- Plain aspirin tablets
- 0.1 M Hydrochloric acid **R** : 34, 37 **S** : 26, 45
- 1 M Sodium hydroxide **R** : 35 **S** : 2, 26, 37, 39
- Borax(AR Grade) **S** : 22, 24, 25
- Phenol red indicator **S** : 22, 24, 25

Preparation of 0.1 M HCl solution

9 mL of concentrated HCl is diluted to 1000 mL using freshly prepared distilled water in a standard volumetric flask.

Preparation of 1 M NaOH solution.

Weigh rapidly approximately 10.5 g of NaOH in a small beaker. Dissolve it in minimum amount of distilled water. Transfer the solution in a 250 mL flask and dilute the solution using boiled out distilled water.

Procedure

Standardisation of HCl

Weigh 0.15 g of Borax accurately and transfer it quantitatively in a clean 250 mL conical flask ; add 50 mL of distilled water to the flask. Titrate the resulting solution with HCl, using methyl red indicator until the colour changes from yellow to red.

- ***Calculate the concentration of the HCl solution.***

Blank titration

Dilute the 25 mL of 1 M NaOH solution in a 250 mL standard flask using freshly boiled distilled water. Pipette out 25 mL of the diluted NaOH solution and titrate it against the HCl solution using phenol red as indicator until the colour changes from red to yellow.

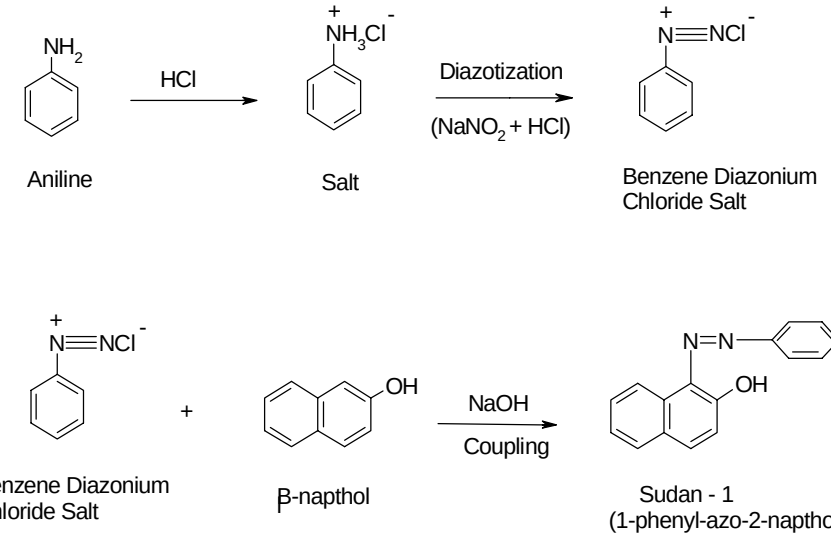
Titration of sample aliquot

Weigh accurately about 1.5 g of the crushed tablet sample and transfer it quantitatively in a 250 mL beaker. Add 25 mL of 1 M NaOH solution with the help of pipette and swirl the content. Boil the mixture gently on a water bath for 15 min and then cool the solution. Transfer the solution to a 250 mL standard flask. Dilute the solution up to the mark with distilled water and mix well. Titrate 25 mL of the diluted solution against the standardised HCl solution using phenol red indicator until the colour changes from red to yellow.

- ***Write down the appropriate chemical reaction for hydrolysis of acetyl salicylic acid.***
- ***Calculate the percentage of aspirin in the sample.***

Problem 26 Synthesis of 1-phenyl-azo-2-naphthol ($C_{16}H_{12}ON_2$)

Reactions



Chemicals and solutions

• Aniline	**R** : 23, 24, 25, 33	**S** : 28, 36, 37, 45
• Concentrated HCl	**R** : 34, 37	**S** : 26, 45
• Solid Sodium Nitrite	**R** : 8, 25	**S** : 44
• β - naphthol	**R** : 20, 22	**S** : 24, 25
• Ethyl Alcohol		
• Urea		**S** : 22, 24, 25
• Sodium Hydroxide	**R** : 35	**S** : 2, 26, 37, 39

Preparation of diazonium salt

Take 1 mL of aniline in a clean 50 mL beaker. Add approximately 5 mL of distilled water to aniline. Place the beaker in an ice-bath. Slowly add 2.5 mL of conc. HCl. Stir the solution with a glass rod to obtain a clear solution. Cool this solution in the ice-bath.

Weigh accurately 0.5 g of sodium nitrite ($NaNO_2$) and transfer it quantitatively in a 15 (or 25) mL test tube. Add 5mL of distilled water (to the test tube) to dissolve $NaNO_2$. Cool the resulting $NaNO_2$ solution in an ice-bath.

Allow both the solutions to attain 0°C temperature. Add sodium nitrite solution in a dropwise manner to the aniline solution with continuous stirring. (During addition, the temperature of the reaction mixture should not rise above 10°C.)

The presence of excess nitrous acid in the reaction mixture is checked using starch iodide paper.

To decompose the excess nitrous acid formed, add a small portion of solid urea. The solution is then filtered. The filtrate contains the diazonium salt.

Coupling reaction

Weigh 0.75 g of powdered β-naphthol in a 50 mL beaker. Add 5 mL of 10% NaOH solution and 5 mL of distilled water to the beaker. Stir well with glass rod to obtain a clear solution. This solution is also cooled in an ice-bath to 0°C.

The ice cooled filtrate containing diazotised salt is added dropwise to the ice cooled solution of β-naphthol with constant stirring. At this stage, an orange-red dye will start precipitating. After the addition of the solution is complete, filter the dye using buchner funnel. Cold water is used for washing the precipitate. Dry the product and record the yield.

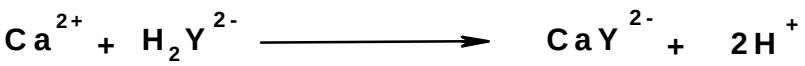
Determination of melting point

Recrystallise a small portion of the organic dye prepared using ethyl alcohol. Gently heat the solution in a water bath (careful!) to dissolve the dye. Filter the hot solution. Cool the filtrate and filter the recrystallised product using Buchner funnel and suction.

- ***Record the weight of the crude product***
- ***Record the melting point of the recrystallised product***.

Problem 27 Determination of calcium in a sample solution

Reaction



Chemical and solutions

- Sample solution containing calcium (prepared from A.R. grade $CaCl_2$) **R** : 36 **S** : 22, 24
- Patton and Reeders indicator

- KOH solution. **R** : 35 **S** : 26, 37, 39, 45
- EDTA disodium salt **R** : 36, 37, 38 **S** : 26, 36

Preparation of 0.01 M EDTA:

Weigh 1.861 g of AR grade Na_2EDTA and quantitatively transfer the same to 500 mL volumetric flask. Add distilled water to the flask to dissolve Na_2EDTA and make up the solution to 500 mL mark with distilled water.

Procedure

Dilute the given sample solution to 100 mL in a 100 mL volumetric flask using distilled water. Pipette out 25 mL of the diluted sample solution in a clean conical flask. Add 25 mL of distilled water and adjust the pH using freshly prepared KOH solution to 12. Check the pH with pH paper. Add a pinch of solid indicator and titrate with Na_2EDTA solution till the colour changes from wine red to blue.

- ***Calculate the amount of calcium in mmoles in 100 mL of the diluted sample*** **solution**

Problem 28 Estimation of methyl ketone by back titration

Methyl ketones like acetone can be estimated by iodinating with excess of standard iodine in an alkaline medium. The unreacted iodine is then back titrated with standard sodium thiosulphate solution.

Chemicals and solutions

- 0.1N Iodine solution **R** : 20, 21 **S** : 23, 25
- 0.1N NaOH **R** : 35 **S** : 2, 26, 37, 39
- Concentrated HCl **R** : 34, 37 **S** : 26, 45
- 1 N H_2SO_4. **R** : 35 **S** : 2, 26, 30
- 0.1 M $Na_2S_2O_3$ **S** : 22, 24, 25

Preparation of 0.1 M $Na_2S_2O_3$:

Weigh 25 g of AR grade $Na_2S_2O_3$ and quantitatively transfer it to a 1 L volumetric flask. Prepare the solution using freshly boiled distilled water. Add 3 drops of chloroform while preparing the solution. Avoid exposure to light.

Preparation of 0.1 N I_2 solution

Dissolve 20 g of iodate-free potassium iodide in 30 - 40 mL of distilled water in a 1 L volumetric flask. Weigh 12.7 g iodine and quantitatively transfer to the concentrated potassium iodide solution. Shake the flask well until all the iodine dissolves and then dilute up to the mark with distilled water.

Procedure

Standardisation of $Na_2S_2O_3$

Weigh out accurately 0.14 to 0.15 g of dry potassium iodate. Dissolve it in 25 mL of distilled and freshly boiled water and add 2 g of iodate free potassium iodide. Add 5 mL of 1N sulphuric acid. Titrate the liberated iodine with thiosulphate solution with constant shaking. When the colour of the solution is pale yellow add 200 mL of distilled water and 2 mL of starch indicator. Continue the titration until the colour changes from blue to colourless.

Determination of ketone

Weigh accurately 0.2 g of the given acetone sample in a clean 50 mL beaker and add minimum amount of distilled water. Transfer the acetone solution to a 250 mL standard volumetric flask. Add distilled water to the flask to prepare acetone solution in water and make up the solution to 250 mL mark with distilled water. Pipette out 10 mL of the acetone solution in a clean conical flask. Add 10 mL of 10% aqueous sodium hydroxide, and stopper the flask. Shake the flask for 10 min. At the end of 10 minutes, add 35 mL of 0.1 N Iodine solution from the burette. Swirl the content, preferably using magnetic stirrer for 5 minutes, and keep it standing for 15 minutes.

Yellow crystals of iodoform will appear. Acidify the solution with H_2SO_4 (check the pH with pH paper).

Titrate the solution against the standardised sodium thiosulphate using starch indicator.

- ***Write down the appropriate chemical reactions for iodination of acetone.***
- ***Calculate the amount of acetone in the given sample solution.***

Problem 29 Determination of phenol in the given sample.

Reactions

$KBrO_3 + 5KBr + 6HCl \rightarrow 6KCl + 3H_2O + 3Br_2 \uparrow$

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2OHBr_3 + 3HBr$

$3Br_2 + 6KI \rightarrow 6KBr + 3I_2 \uparrow$

$6Na_2S_2O_3 + 3I_2 \rightarrow 3Na_2S_2O_3 + 6NaI$

Chemicals and solutions

- 0.3g phenol **R** : 24, 25, 34 **S** : 2, 28, 44
- 0.02M $KBrO_3$ **R** : 9 **S** : 24, 25, 27
- 3M H_2SO_4 **R** : 35 **S** : 2, 26, 30
- KBr
- KI **S** : 22, 24, 25
- 1 M $Na_2S_2O_3$ **S** : 24, 25, 28
- Starch indicator.

Preparation of 0.1 M $Na_2S_2O_3$

Weigh 25 g of AR grade $Na_2S_2O_3$ in a small beaker. Quantitatively transfer it to a 1 L volumetric flask. Prepare the solution using freshly boiled distilled water. Add 3 drops of chloroform while preparing the solution. Avoid exposure to light.

Standardisation of $Na_2S_2O_3$

Weigh out accurately 0.14 to 0.15 g of dry potassium iodate. Dissolve it in 25 mL of fresh, boiled distilled water and add 2 g of iodate free potassium iodide. Add 5 mL of 1N sulphuric acid. Titrate the liberated iodine with thiosulphate solution with constant shaking. When the colour of the solution is pale yellow add 200 mL of distilled water and 2 mL of starch indicator. Continue the titration until the colour changes from blue to colourless.

Procedure

Dissolve the given sample of phenol to 250 mL with distilled water. Take 25 mL of the phenol solution into 250 mL stoppered conical flask. Add 25 mL of standard potassium bromate solution and 0.5 g of potassium bromide. Add 5 mL of 3M sulphuric acid. Stopper the flask immediately. Mix the reagents and let them stand for 15 min (avoid exposure to light). Then, add 2.5 g of potassium iodide rapidly. Re-stopper the flask immediately and swirl the contents of the flask to dissolve the solid.

Titrate the liberated iodine with standard 0.1M $Na_2S_2O_3$ from the burette using starch indicator.

- ***Calculate the amount of phenol per 250 mL of the solution.***

Problem 30 Determination of amount of Fe (III) present in the given sample

Fe (III) in the sample solution is first reduced to Fe (II) in HCl medium using stannous chloride. Excess of stannous chloride is oxidized by addition of mercury (II) chloride. The Fe(II) is then titrated with standard potassium dichromate solution.

Chemicals and solutions

• Sample solution	**R** : 36, 38	**S** : 26, 36
• 0.1N $K_2Cr_2O_7$ solution	**R** : 45, 36, 37, 38, 43	**S** : 53, 22, 28
• Equimolar H_2SO_4 &	**R** : 35	**S** : 2, 26, 30
H_3PO_4 acid mixture	**R** : 34	**S** : 26, 45
• Conc. HCl	**R** : 34, 37	**S** : 26, 45
• 5% $HgCl_2$	**R** : 26, 27, 28	**S** : 13, 28, 45
• 3% $SnCl_2$ solutions	**R**: 22, 36, 37, 38	**S** : 26, 36,
• Diphenylamine indicator.	**R** : 23, 24, 25, 33	**S** : 28, 36, 37, 45

Note : $NH_4Fe(SO_4)_2.12H_2O$ is used to prepare the sample solution

Preparation of 0.1N $K_2Cr_2O_7$ solution

Weigh accurately 1.225 g of pure $K_2Cr_2O_7$ and transfer it to a 250 mL volumetric flask. Prepare the solution using distilled water.

Procedure:

Dilute the given Fe(III) sample solution to 100 mL using the standard volumetric flask. Take 10 mL of the diluted sample solution in a clean conical flask. Add 2 mL of concentrated HCl and boil the solution. To the hot solution, add $SnCl_2$ solution dropwise till the reaction mixture becomes colourless. Add 2 - 3 drops of $SnCl_2$ in excess.

Cool the solution under tap water. Add 2 to 3 mL of $HgCl_2$ solution at once. A white precipitate is obtained at this stage. (If grey precipitate is obtained, reject the sample and start again.)

Add 2 to 3 mL of the acid mixture and 1 drop of the diphenylamine indicator and titrate it against $K_2Cr_2O_7$ solution. Continue the titration until a colour change from colourless to permanent blue or violet is observed.

- ***Write down the appropriate chemical reactions .***
- ***Calculate the amounts of Fe (III) and $NH_4Fe(SO_4)_2 12H_2O$ per 100 mL of the sample solution.***