27th INTERNATIONAL CHEMISTRY OLYMPIAD
PRACTICAL EXAMINATION

FRIDAY, JULY 14,1995

Please read the entire procedure and the Student's Report before beginning the experiment.

WARNING: You must wear your safety goggles in the Laboratory and use the pipette bulbs provided. Should you remove your goggles, or pipette by mouth, you will be given a warning. A second warning will result in a five point penalty. A third warning will result in removal from the laboratory. Removal from the laboratory will result in a zero mark for the practical examination.

NOTES:

1) Write your name, student number (see student's No. on the table) and the delegation at the top of each student's report sheet.
2) Begin only after the instructor has given a START message.
3) You will be given 5 hours to finish the whole practical exam, including writing your report.
4) All the answers are to be written on the student's report sheets within the blanks provided. Only those answers given on the correct positions will be taken into consideration.
5) Write your report with the ballpen provided.
6) Use deionized water except for cooling.
7) The significant figures should be used properly.

***A*r of some elements**

H	1.008	S	32.06
C	12.01	K	39.10
N	14.01	Cu	63.54
O	16.00	I	126
Na	22.99		

PRACTICAL PROBLEM I

Identification of Unknown Solutions

Reagents

H_2SO_4 (conc.)	H_2SO_4 (6 mol·dm^{-3})
HNO_3(conc.)	HNO_3 (6 mol·dm^{-3})
HCl(conc.)	HCl (6 mol·dm^{-3})
$Ba(OH)_2$(satd.)	NaOH (6 mol·dm^{-3})
$BaCl_2$(0.5 mol·dm^{-3})	$Ba(NO_3)_2$(0.5 mol·dm^{-3})

Desk equipments

One test tube holder
five small test tubes

Problem

You are supplied with five different solutions contained in five test tubes labeled as A,B,C,D and E, respectively. The solution, in each test tube, contains one of the following compounds

NH_4Cl, $(NH_4)_2SO_4$, $NaNO_3$, $MgCl_2$, Na_2SO_4

Identify these solutions.

NOTES:

(1) You can only select the provided reagents and use a procedure as simple as possible to complete your task. You are getting a mark not only according to the correct identification, but also to the number of steps you have taken.
(2) You have to carry out the whole analysis by using the provided amount of these unknown solutions. Supplement of them will be available, but it will reduce the mark you obtain.

PRACTICAL PROBLEM II

Preparation of cis-Copper-bis-Glycinate Hydrate [$Cu(gly)_2 \cdot xH_2O$]

Copper(II) amino acidate coordination compounds are monometric units for synthesizing important biopolymers such as metalloenzymes like ceruloplasmin, on which every living organism depends. In laboratory cis-copper-bisglycinate hydrate can be produced by the reaction of cupric hydroxide with glycine at a temperature of *ca.* 70°C.

Reagents:

$CuSO_4 \cdot 5H_2O$(s)
$NH_3 \cdot H_2O$(3 mol·dm^{-3})
glycine(s)
95% ethanol,
acetone
NaOH(2 mol·dm^{-3})
$BaCl_2$(0.5 mol·dm^{-3})

Desk equipments

beaker 250 cm^3 ×4
graduated cylinder 100cm^3 ×1
filter flask (shared)
Buchner funnel 60mm ×1
watch glass ×2
dropper ×2
spatula ×1
glass stirring rod ×1
aspirator
thermometer (at least 100° C)

Procedure:

1. Preparation of $Cu(OH)_2$

(1) Dissolve your pre-weighted sample of $CuSO_4 \cdot 5H_2O$ (6.0 g) in 40 cm^3 of water with a 250 cm^3 beaker as a container.

(2) Add slowly 3 mol·dm^{-3} ammonia solution to the $CuSO_4$ solution, gently stirring, until the precipitate is completely dissolved and the solution is turning blue-violet.

(3) Add 2 mol·dm^{-3} NaOH solution to the above solution until no more precipitate formed.

(4) Filter the precipitate over a Buchner funnel under reduced pressure. Wash the precipitate with water until no SO_4^{2-} ion is detected in the filtrate.
(5) Collect $Cu(OH)_2$ for the preparation of $Cu(gly)_2 \cdot xH_2O$.

Write the equations for the main chemical reactions having taken place in the above procedure.

2. Preparation of cis-copper-bisglycinate hydrate
(1) Dissolve a pre-weighted sample of glycine (3.6 g) in 130 cm^3 of water and then warm the solution in a hot water bath(70°C). Add the $Cu(OH)_2$ to the solution, gently stirring until the precipitate is dissolved. Perform a hot filtration and add 10 cm^3 of 95% ethanol.
(2) Cool the solution and then needle-like crystals appear, place it in the ice water bath for 10 min.
(3) Filter the crystals over a Buchner funnel under reduced pressure, wash once with 10 cm^3 of ethanol-water mixing solvent and then twice with 10 cm^3 acetone, squeeze the crystals as dry as possible on the funnel.
(4) Collect the crystals to a watch glass and dry it (consult your supervisor).
(5) Half an hour later weigh the product. Write the mass of product and the percentage of yield on your student's report. Give the expressions for calculation to show how you calculate.

PRACTICAL PROBLEM III

Determination of copper(II) content in $Cu(gly)_2 \cdot xH_2O$

The Cu(II) content in $Cu(gly)_2 \cdot xH_2O$ crystals prepared yourself can be determined by iodometry with starch solution as indicator. Based on the data obtained one can calculate the moles of hydrates of crystals in $Cu(gly)_2 \cdot xH_2O$.

Reagents

Standard KIO_3 (see the label on the bottle to get the accurate concentration)
H_2SO_4(1.0 mol $\cdot$dm^{-3}) as indicator.
KI(0.6 mol $\cdot$dm^{-3})
KSCN(2 mol $\cdot$dm^{-3})
Starch(0.5%)
$Na_2S_2O_3$ (to be standardized)

Desk equipments

buret 50cm^3 ×1
pipette 25cm^3 ×1
pipette bulb
beakers (dry) 100cm^3 ×2
volumetric flask 100cm^3 ×1
Erlenmeyer flask 250 cm^3 ×3
graduated cylinder 10cm^3 ×3, 100cm^3 ×1
wash bottle
single pan balance (shared)
hot water bath (shared)

Procedure

1. Standardization of $Na_2S_2O_3$ solution
(1) Transfer 25.00 cm^3 of standard KIO_3 solution to an Erlenmeyer flask.
(2) Add 5 cm^3 of water, 10 cm^3 of KI solution and 5 cm^3 of H_2SO_4 (1.0 mol$\cdot$dm^{-3}) to the flask.
(3) Titrate immediately with $Na_2S_2O_3$ solution.
(4) Add 2 cm^3 starch solution when the colour of the titrand turns pale yellow.
(5) Continue titrating until the blue color of the solution disappears.
(6) Proceed with step (1)—(5) twice parallely.

2. Determination of Cu(II) content in $Cu(gly)_2 \cdot xH_2O$

(1) Weigh 1.0—1.2 g (precision of ±0.0002 g) of $Cu(gly)_2 \cdot xH_2O$ with a dry 100 cm^3 beaker as the container.

(2) Dissolve it with 40 cm^3 of water and 8 cm^3 of H_2SO_4(1.0 $mol \cdot dm^{-3}$).

(3) Transfer the above solution quantitatively to a 100 cm^3 volumetric flask and dilute to the mark.

(4) Transfer 25.00 cm^3 of the Cu(II) Solution to an Erlenmeyer flask, add 50 cm^3 of water and 10 cm^3 of KI solution to the flask.

(5) Titrate immediately with standardized $Na_2S_2O_3$ solution.

(6) Add 2 cm^3 of starch solution and 3 cm^3 of KSCN solution to the flask when the colour of the titrand turns from brown to pale yellow.

(7) Titrate continuously until the blue color of the solution disappears.

(8) Proceed with steps (4)— (7) twice parallelly.

Name

Student's No.

Delegation

Student's Report for Practical Problem I

1.Identification of unknown solutions

labels of solutions	A	B	C	D	E
chemical formulae					

2. Equations for chemical reactions taking place in each experimental step

step one (with the first reagent you choose)

step two (with the second reagent you choose)

step three (with the third reagent you choose)

If you proceed with more steps, write the corresponding chemical equations continuously.

Name

Student's No.

Delegation

Student's Report for Practical Problem II

1. Equations for the main chemical reactions having taken place in the preparation of $Cu(OH)_2$.

2. Mass of $Cu(gly)_2 \cdot xH_2O$ = (g)

Percent yield

The expression for calculation

Name

Student's No.

Delegation

Student's Report for Practical
Problem III

1. Standardization of $Na_2S_2O_3$ Solution
1) The two equations for chemical reactions taking place during the standardization of $Na_2S_2O_3$.

i

ii.

(2) Volumes of $Na_2S_2O_3$ Solution

V_1= cm^3 V_2= cm^3
V_3= cm^3

V(mean value)= cm^3

(3) Concentration of $Na_2S_2O_3$= mol·dm^{-3}

Expression for the calculation:

2. Determination of Cu(II) in $Cu(gly)_2 \cdot xH_2O$
(1) Chemical equation for the reaction between Cu^{2+} and I^-

(2) Mass of $Cu(gly)_2 \cdot xH_2O$ = g

3) Volumes of $Na_2S_2O_3$ solution

V_1= cm^3 V_2= cm^3 V_3= cm^3

V(mean value)= cm^3

(4) Mass % of Cu(II) in $Cu(gly)_2 \cdot xH_2O$ = %
Expression for the calculation:

(5) X Value in $Cu(gly)_2 \cdot xH_2O$

X = (with precision of 0.01)

Expression for the calculation:

Results key for practical problem I
(10 pts)

1. Identification of unknown solutions (5 pts)

labels of solutions	A	B	C	D	E
chemical formulae					

1 pt for one correct identification

2. Equations for chemical reactions taking place in each experimental step

5 pts

Step one

I $2\ NH_4Cl + Ba(OH)_2 = BaCl_2 + 2NH_3 \cdot H_2O$

or $NH_4^+ + OH^- = NH_3 \cdot H_2O$

ii $(NH4)_2SO_4 + Ba(OH)_2 = 2NH_3 \cdot H_2O + BaSO_4 \downarrow$

or $2NH_4^+ + SO_4^{2+} + Ba^{2+} + 2OH^- = 2NH_3 \cdot H_2O + BaSO_4 \downarrow$

iii $MgCl_2 + Ba(OH)_2 = BaCl_2 + Mg(OH)_2 \downarrow$

or $Mg^{2+} + OH^- = Mg(OH)_2 \downarrow$

iv $Na_2SO_4 + Ba(OH)_2 = 2NaOH + BaSO_4 \downarrow$

or $SO_4^{2-} + Ba^{2+} = BaSO_4 \downarrow$

Step two

$NH_3 + HCl = NH_4Cl$

5 pts for using $Ba(OH)_2$ and HCl or $Ba(OH)_2$ only

3 pts for using more than these two reagents

for one incorrect equation (-1pt)

Results key for practical problem II
(12 pts)

1. Equations for the main chemical reactions having taken place in the preparation of $Cu(OH)_2$ (2 pts)

$Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$

$Cu(NH_3)_4^{2+} + 2OH^- = Cu(OH)_2 + 4NH_3$

one pt for one correct equation

2. Mass of $Cu(gly)_2 \cdot xH_2O$ = (g)

mass ≥2.6g	(8 pts)
2.6 > mass≥2.2	(6 pts)
2.2 > mass ≥1.5	(4 pts)
1.5 > mass ≥1.1	(2 pts)
1.0 > mass ≥ 0.5	(1 pt)
dripping	(0 pt)

Percent yield

The expression for calculation

Results key for practical problem III (20 pts)

1. Standardization of $Na_2S_2O_3$ solution (10 pts)

(1) The two equations for chemical reactions taking place during the standardization of $Na_2S_2O_3$. (2 pts)

i $IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$

or $8I^- + IO_3^- + 6H = 3I_3^- + 3H_2O$

ii $I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$

or $I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}$

1 pt for one correct equation. (incorrect balance -0.5 pt)

(2) Volumes of $Na_2S_2O_3$ solution (4 pts)

V_1= cm^3 V_2= cm^3

V_3= cm^3

V(mean value)= cm^3

1 pt for correct significant figures

3 times of titration (1 pt)

two or one titration (0 pt)

precision ≤ 0.04 cm^3 (2 pts) (maximum-minimum)

0.04 cm^3 < precision ≤0.08 cm^3 (1 pt)

(3) Concentration of $Na_2S_2O_3$ mol·dm^{-3} (4 pts)

correct significant figures (1 pt)

error ±0.00015 — ±0.00020 mol.dm^{-3} (3 pts)

±0.00021 — ±0.00025 mol.dm^{-3} (2 pts)

±0.00026 — ±0.00030 mol.dm^{-3} (1 pt)

2. Determination of Cu(II) in $Cu(gly)_2 \cdot xH_2O$ (10 pts)

(1) Chemical equation for the reaction between Cu^{2+} and I^-

$2Cu^{2+} + 4I^- = 2CuI + I_2$ **(1 pt)**

(2) Mass of $Cu(gly)_2 \cdot xH_2O$ = g (1 pt)

(3) Volumes of $Na_2S_2O_3$ (4 pts)

correct significant figures (1 pt)

3 times of titration (1 pt)

precision ≤ 0.04 cm^3 (2pts)

0.04cm^3<precision≤0.08cm^3 (1pt)

(4) Mass % of Cu^{2+} in $Cu(gly)_2 \cdot xH_2O$ =27.66%(Theo.) (1 pt)

mass % >29% or mass %<26% (0 pt pts)

(5) Calculation of x in $Cu(gly)_2 \cdot xH_2O$ (4 pts)

x = 1.00 (Theo.)

the ranges of x:

1.00±(0.00 — 0.10) (4 pts)

1.00±(0.11 — 0.15) (3 pts)

1.00±(0.16 — 0.20) (2 pts)

1.00±(0.21 — 0.25) (1 pts)