45th National Chemistry Olympiad

Maastricht University

PRACTICAL TEST

Marking scheme

Thursday June 6, 2024

Experiment 1 The determination of the amount of crystal water (x) in a mixture of $Na_2CO_3.xH_2O$ and $NaHCO_3$ — 40 points

Maximum score 10
The following practical skills are assessed:
- safety, working clean and independence
- handling of the glassware

□1 Maximum score 8
- mass of the sample and the molarity of the hydrochloric acid — 1
- burette readings read in two decimals — 2
- difference between the two duplicates of the titrations — 5

The score points for the differences between the two duplicates for each titration are determined as follows:

If the difference in the used volume between the duplicates ≤ 0.10 mL	5
If 0.10 mL < the difference in the used volume between the duplicates ≤ 0.20 mL	4
If 0.20 mL < the difference in the used volume between the duplicates ≤ 0.30 mL	3
If 0.30 mL < the difference in the used volume between the duplicates ≤ 0.50 mL	2
If 0.50 mL < the difference in the used volume between the duplicates ≤ 0.70 mL	1
If the difference in the used volume between the duplicates > 0.70 mL	0

The final score is the average of the scores for both titrations.

□2 Maximum score 4
Titration with phenolphtalein:
$CO_3^{2-} + H_3O^+ \rightarrow HCO_3^- + H_2O$
Titration with methyl orange:
$CO_3^{2-} + 2\ H_3O^+ \rightarrow CO_2 + 3\ H_2O$ and $HCO_3^- + H_3O^+ \rightarrow CO_2 + 2\ H_2O$

- correct reaction equation for the titration with phenolphtalein — 1
- for the titration with methyl orange, correct reaction equation with the carbonate — 2
- for the titration with methyl orange, correct reaction equation with the hydrogen carbonate — 1

Remarks
- *When H^+ is used instead of H_3O^+, in an otherwise correct equation, accept this as correct.*
- *When for the titration with methyl orange the equations $CO_3^{2-} + H_3O^+ \rightarrow HCO_3^- + H_2O$ and $HCO_3^- + H_3O^+ \rightarrow CO_2 + 2\ H_2O$ are given, accept this as correct.*
- *When H_2CO_3 is written after the arrow in the equations for the titration with methyl orange, do not penalize this.*

□3 Maximum score 10

From the titration with phenolphthalein follows that $V_1 \times 0.1000$ mmoles of $Na_2CO_3.xH_2O$ were present in 25.00 mL of the solution from the volumetric flask,

So $\frac{V_1 \times 0.1000}{25.00} \times 250.00$ mmoles of $Na_2CO_3.xH_2O$ were present in the sample.

$V_2 \times 0.1000$ mmoles of H_3O^+ reacted in the titration with methyl orange. Of this amount $2 \times V_1 \times 0.1000$ mmoles reacted with $Na_2CO_3.xH_2O$, so the amount of mmoles of $NaHCO_3$ in 25.00 mL of the solution of the sample from the volumetric flask was

$V_2 \times 0.1000 - 2 \times V_1 \times 0.1000$, so $\frac{V_2 \times 0.1000 - 2 \times V_1 \times 0.1000}{25.00} \times 250.00$ mmoles of $NaHCO_3$ were present in the sample.

- calculation of the amount of mmoles of H_3O^+ that reacted in both titrations: $V_1 \times 0.1000$ and $V_2 \times 0.1000$, respectively — 1
- calculation of the amount of mmoles of $Na_2CO_3.xH_2O$ in the 25.00 mL solution:. equals $V_1 \times 0.1000$ — 1
- notion that in the titration with methyl orange $2 \times V_1 \times 0.1000$ mmoles of $Na_2CO_3.xH_2O$ reacted — 1
- calculation of the amount of mmoles of $NaHCO_3$ in the 25.00 mL solution — 1
- conversion from the amount of mmoles of $Na_2CO_3.xH_2O$ and $NaHCO_3$ in the 25.00 mL solution to the amount of mmoles of $Na_2CO_3.xH_2O$ and $NaHCO_3$ in the sample: divide by 25.00 and multiply by 250.00 — 1
- results — 5

□4 Maximum score 4

The amount of mg of H_2O in the sample is

$$m_{sample} - m_{Na_2CO_3} - m_{NaHCO_3} = m_{sample} - \text{mmoles of } Na_2CO_3 \times 105.99 - \text{mmoles of } NaHCO_3 \times 84.007$$

Thus, the amount of mmoles of H_2O in the sample is:

$$\frac{m_{sample} - \text{mmol } Na_2CO_3 \times 105.99 - \text{mmol } NaHCO_3 \times 84.007}{18.015}.$$

And $x = \frac{\text{amount of mmoles of } H_2O}{\text{amount of mmoles of } Na_2CO_3}$.

- calculation of the amount of mg of Na_2CO_3 in the sample and of the amount of mg of $NaHCO_3$ in the sample — 1
- calculation of the amount of mg of H_2O in the sample — 1
- calculation of the amount of mmoles of H_2O in the sample — 1
- calculation of x — 1

▫5 Maximum score 4

An example of a correct answer is:

A solution of barium hydroxide can be used. Then HCO_3^- from the $NaHCO_3$ as well as CO_3^{2-} from the $Na_2CO_3.xH_2O$ will react to $BaCO_3$. In that case the titration with methyl orange does not have to be executed.

- use of a solution of barium hydroxide 1
- CO_3^{2-} from $Na_2CO_3.xH_2O$ reacts to $BaCO_3$ 1
- HCO_3^- from $NaHCO_3$ reacts to $BaCO_3$ 1
- conclusion 1

If an answer is given as: „A solution of barium chloride can be used. Then, CO_3^{2-} from $Na_2CO_3.xH_2O$ reacts to $BaCO_3$. The titration with fenolftalein does not have to be executed.” 2

Remark

When an answer is given as: „A solution of barium chloride can be used. Then, CO_3^{2-} from $Na_2CO_3.xH_2O$ reacts to $BaCO_3$. Because of that, the equilibrium of HCO_3^- will completely shift into the direction of CO_3^{2-} , that will be converted into $BaCO_3$ thereafter. Thus, the titration with methyl orange does not have to be executed.”, do not penalize this.

Experiment 2 Kinetic study of the decomposition of tris-(oxalato)-manganese(III) ion — 40 points

Maximum score 10

The following practical skills are assessed:

- safety, working clean and independence
- handling of the glassware

□6 Maximum score 2

- times noted in sec 1
- absorbances noted 1

□7 Maximum score 2

- calculation of ΔA and Δt in both variants 1
- calculation of s_I and s_{II} 1

□8 Maximum score 8

- calculation of $\log s_1$ and $\log s_2$ 1
- calculation of $\log [\{Mn(C_2O_4)_3\}^{3-}]_I$ and $\log [\{Mn(C_2O_4)_3\}^{3-}]_{II}$ 1
- calculation of n 1
- result 5

□9 Maximum score 2

- answer in accordance with the calculated value of n 1
- motivation 1

□10 Maximum score 3

- calculation of ΔA, three times 1
- calculation of Δt, three times 1
- calculation of s, three times 1

□11 Maximum score 9

- calculation of the concentration of the complex at the start of each time interval 1
- calculation of the value of k, four times 1
- calculation of the average k 1
- correct dimension for k 1
- result 5

□12 Maximum score 4

An example of a correct answer is:

(4.0 × 0.020 =) 0.080 mmoles of MnO_4^- and (2.0 × 0.20 =) 0.40 mmoles of Mn^{2+} and (14.0 × 0.20 =) 28 mmoles of $H_2C_2O_4$ are added together.

So the amount of MnO_4^- (is the limiting factor and) determines the amount of the complex ion that is formed.

So 5 × 0.080 = 0.40 mmol complex is formed in (4.0 + 2.0 + 14.0 =) 20.0 mL solution.

The concentration is $\frac{0.40}{20} = 0.020$ mol L^{-1}.

- calculation of the amount of mmoles of MnO_4^-, Mn^{2+} and $H_2C_2O_4$ 1
- conclusion that the amount of mmoles of MnO_4^- determines the amount of mmoles of complex ion that is formed 1
- calculation of the amount of mmoles of complex ion that is formed 1
- calculation of the concentration of the complex ion at t = 0 1