The 2nd Olympiad of Metropolises

Chemistry

Grading Scheme and Answers to Practical Problems

September 5, 2017

Moscow, Russia

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).

Question	M.V., mL	A, mL	B, mL	y, mL	z, mL	Max grade
1.1	See on a separate sheet	M.V.-0.1	M.V.+0.1	M.V.-1.0	M.V.+1.0	13 points
1.2.	See on a separate sheet	M.V.-0.15	M.V.+0.15	M.V.-1.00	M.V.+3.00	13 points
1.3	See on a separate sheet	M.V.-0.3	M.V.+0.3	M.V.-2.0	M.V.+2.0	14 points

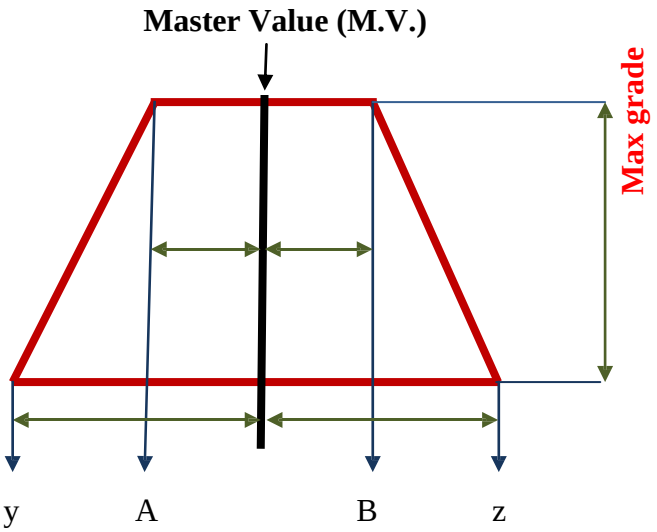
If A< Value < B, then Grade = Maxgrade

If Value < y, then Grade = 0, If Value > z, then Grade = 0

If y < Value < A, then Grade = Max grade × (Value – y)/(A – y)

If B < Value < z, then Grade = Max grade × (z – Value)/(z – B)

Value is the result reported by the student.



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

c = **0.150 M**

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

$5Fe(CN)_6^{4-} + MnO_4^- + 8H^+ = 5Fe(CN)_6^{3-} + Mn^{2+} + 4H_2O$

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

c (initial) = $\boldsymbol{c_{Mn} = c_{FeCy_6} V_{FeCy_6} / V_{Mn} = 0.150\ M \cdot 5.0\ mL / 5V_{Mn} = \sim 0.02\ M,}$

where 5 is equivalence factor.

c (diluted) = $\boldsymbol{c}$ **(initial) × 5 mL / 100 mL = ~0.001 M**

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

1. **$Zn + 2H^+ = Zn^{2+} + H_2$**
2. **$Zn + Fe^{3+} = Zn^{2+} + Fe^{2+}$**

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

Without the reduction:

$\boldsymbol{c_{Fe(II)} = 5c_{Mn}V_{Mn(1)} / V_{Fe} = 5 \cdot 0.99 \cdot 10^{-3}\ M \cdot V_{Mn(1)} / 10.0\ mL}$

After reduction:

$\boldsymbol{c_{Fe(total)} = 5c_{Mn}V_{Mn(2)} / V_{Fe} \times V_{flask}/V_{aliquot} =}$

$\boldsymbol{= 5 \cdot 0.99 \cdot 10^{-3}\ M \cdot V_{Mn(2)} / 10.0\ mL \times 50\ mL / 30\ mL}$

$\boldsymbol{c_{Fe(III)} = c_{Fe(total)} - c_{Fe(II)}}$

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:

$2MnO_4^- + 10Cl^- + 16H^+ = Mn^{2+} + 5Cl_2$ (или до HOCl) $+ 8H_2O$

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

$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$

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: **see equation 2.1.**

In the presence of Fe(II): $\mathbf{MnO_4^- + 3Fe^{2+} + 8H^+ = Mn(IV) + 3Fe^{3+} + 4H_2O}$

$$\mathbf{Mn(IV) + 2Cl^- = Mn^{2+} + Cl_2}$$

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**):

$$\mathbf{Mn(IV) + 6F^- = MnF_6^-}$$

$$\mathbf{MnF_6^- + Cl^- - no\ reaction}$$

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).

1.1. Synthesis

The grading scheme takes into account two values re-measured by the Jury: mass of the product (m, g) and its refraction index (n_D). A correcting factor based on the latter is applied to a student's points obtained for the yield.

Parameter	M.V.	A	B	y	z	Max grade
Mass	7.7 g	6 g	8.2 g	0 g	10 g	36 points
n_D	1.3960	1.3955	1.3965	1,3333	1.4240	1

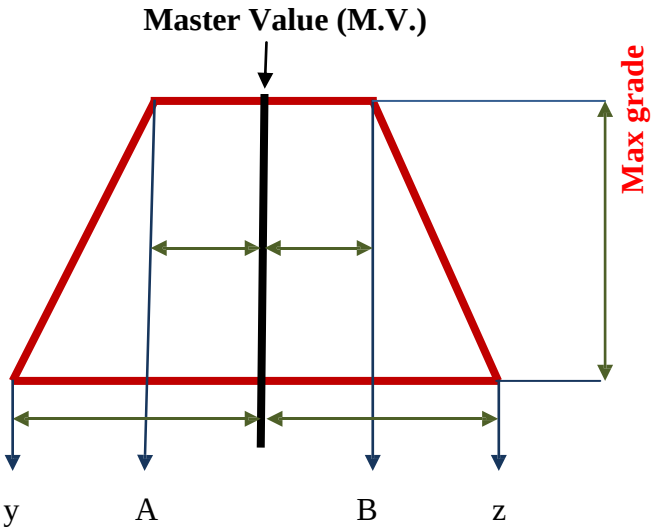
If A< Value < B, then Grade = Maxgrade

If Value < y, then Grade = 0, If Value > z, then Grade = 0

If y < Value < A, then Grade = Max grade × (Value – y)/(A – y)

If B < Value < z, then Grade = Max grade × (z – Value)/(z – B)

Values are the results re-measured by the lab assistants.

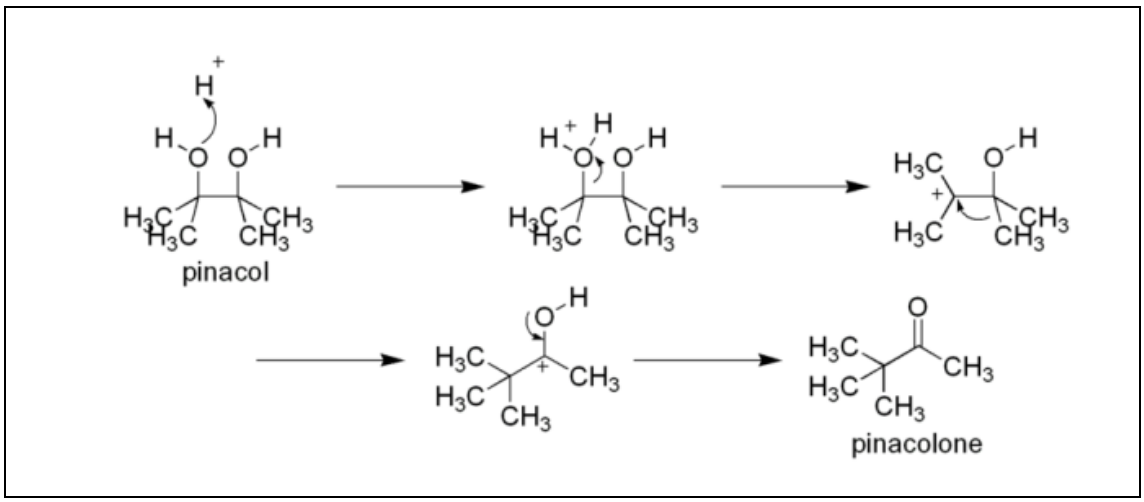


Students result = Grade of mass * Correcting factor (n_D)

Weighing skills: 2 points if a student's result differs from the re-weighed value not more than by 0.2%.

Correct calculation of yield: 2 point.

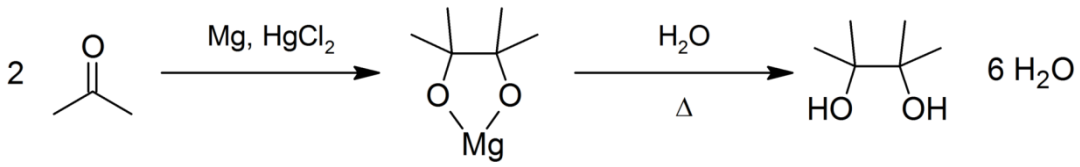
2.1. Write down the mechanism of the pinacol-pinacolone rearrangement:



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.