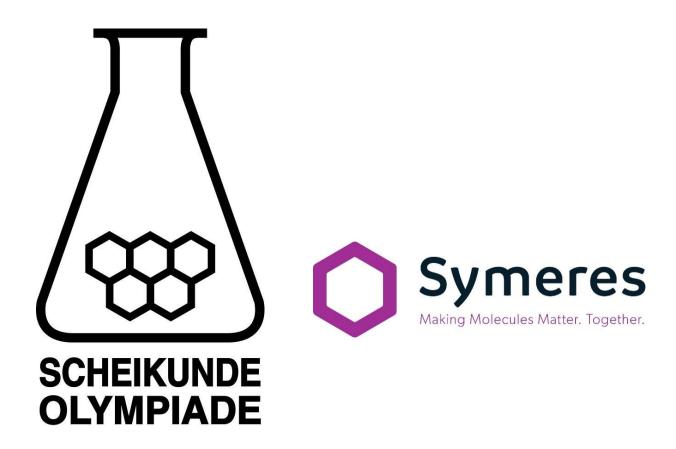
NATIONAL CHEMISTRY OLYMPIAD 2025

MARKING SCHEME PRELIMINARY ROUND 2 To be held between 17th and 25th March 2025



- This preliminary round consists of 20 multiple choice questions divided over 8 topics, and 3 problems with a total of 16 open questions.
- The maximum score for this paper is 98 points.
- Required materials: (graphic) calculator and BINAS 6th or 7th edition or ScienceData 1st edition or BINAS 5th edition, English version.
- The total number of points available for each question is stated.
- The attached marking scheme must be used when grading the work. In addition, the general rules for the Dutch Central Exams apply.

Problem 1 Meerkeuzevragen

(total 40 points)

For every correct answer: 2 points

Brief summary

| nr. | answer |
|--------------------------------------|-------------|
| 1 | С |
| 2 | С |
| 3 | D A |
| 4 | A |
| 5 | D |
| 6 | E |
| 1 2 3 4 5 6 7 8 | D |
| 8 | D A B |
| 9 | В |
| 10 | С |
| 11 | С |
| 12 | E A C |
| 13 | A |
| 14 | С |
| 15 | D |
| 16 | D C D |
| 17 | С |
| 18 | D |
| 19 | С |
| 20 | D |

Carbon chemistry

1 C If the ozone molecule approaches from 'above' in case I, the molozonide depicted in the question is formed.

If the ozone molecule approaches from 'below', o is for

and that is the mirror image of the molozonide drawn in the question.

Also in case II, the ozone molecule can approach from two sides, and then it forms

These formulas are identical.

- 2 C $H_3C \longrightarrow CH_3$ $H_3C \longrightarrow H$ $H_3C \longrightarrow CH_3$ $H_3C \longrightarrow CH_3$
- 3 D **

The C atom indicated with an asterisk is asymmetric, so there are two variants of this structure.

Rate of reactions and equilibrium

4 A 5.00 g NO_2 is $\frac{5.00}{46.006}$ mol; at 310 K and a volume of 1.00 dm³, the pressure is

$$p_{NO_2} = \frac{5.00}{46.006} \times \frac{8.314 \times 310}{1.00 \cdot 10^{-3}} = 2.80 \cdot 10^5 \text{ Pa}.$$

$$N_2O_4$$
 \rightleftharpoons 2 NO_2

initial 0 2.80·10⁵ Pa

change + x Pa - 2x Pa equilibrium x Pa $(2.80 \cdot 10^5 - 2x) Pa$

The equilibrium pressure is $2.80 \cdot 10^5 - 2x + x = 2.80 \cdot 10^5 - x = 1.71 \cdot 10^5$ Pa.

Thus $x = 1.09 \cdot 10^5$ Pa.

Thus $p_{\mathrm{NO_2}} = 2.80 \cdot 10^5 - 2 \times 1.09 \cdot 10^5 = 0.62 \cdot 10^5$ Pa and $p_{\mathrm{N_2O_4}} = 1.09 \cdot 10^5$ Pa.

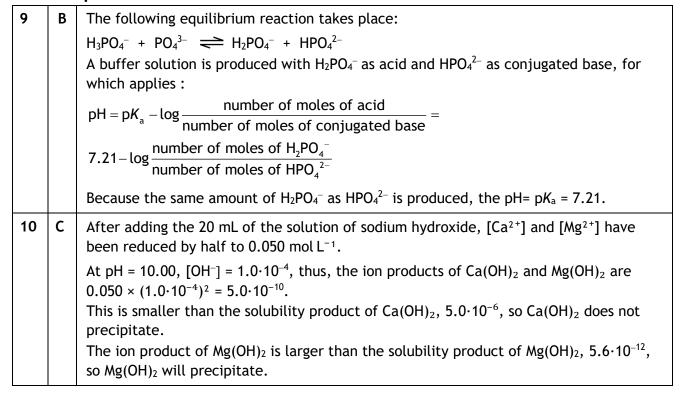
Thus $K_p = \frac{(p_{NO_2} / p_0)^2}{p_{N_2O_4} / p_0} = \frac{(0.62 \cdot 10^5 / 10^5)^2}{1.09 \cdot 10^5 / 10^5} = 0.35$.

| 5 | D | The rate of the total reaction is determined by the slowest (second) step, therefore $r = k_2[\text{Cl}][\text{N}_2\text{O}]$. For the first step, it applies that $K = \frac{[\text{Cl}]^2}{[\text{Cl}_2]}$, thus $[\text{Cl}] = \sqrt{K \times [\text{Cl}_2]}$, thus $r = k_2[\text{N}_2\text{O}]\sqrt{K \times [\text{Cl}_2]}$, or $r = k_2K^{1/2}[\text{N}_2\text{O}][\text{Cl}_2]^{1/2} = k[\text{N}_2\text{O}][\text{Cl}_2]^{1/2}$. |
|---|---|---|
| | | $I = \kappa_2[N_2 \cup J_1] \wedge \kappa_2[N_1 \cup J_2 \cup J_2] = \kappa[N_2 \cup J_2] \cup I_2 \cup I_2$ |
| 6 | E | $K_1 = \frac{[NO]^2}{[N_2][O_2]}$ |
| | | $K_{1} = \frac{[NO]^{2}}{[N_{2}][O_{2}]}$ $K_{2} = \frac{[NO_{2}]^{2}}{[NO]^{2}[O_{2}]}$ $K_{3} = \frac{[N_{2}O_{3}]}{[NO][NO_{2}]}$ |
| | | $K_3 = \frac{[N_2O_3]}{[NO][NO_2]}$ |
| | | $K = \frac{[N_2]^2[O_2]^3}{[N_2O_3]^2} = \frac{[N_2]^2[O_2]^2}{[NO]^4} \times \frac{[NO_2]^2[O_2]}{[NO_2]^2} \times \frac{[NO]^2[NO_2]^2}{[N_2O_3]^2} = \frac{1}{K_1^2 \times K_2 \times K_3^2}$ |

Structures and formulae

| 7 | D | They both have the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$. |
|---|---|--|
| 8 | A | F is the most electronegative halogen atom and makes the OH bond the most polar at a distance. |

pH / acid-base



Redox and electrolysis

| 11 | O | The three Fe^{2+} ions donate a total of three electrons. The oxygen molecule gains four electrons. To make them equal to each other, the coefficient of $Fe_3(PO_4)_2$ is multiplied by 4 and that of O_2 by 3. |
|----|---|--|
| | | The reaction equation becomes: |
| | | $4 \text{ Fe}_3(PO_4)_2 + 3 O_2 + 6 H_2O \rightarrow 8 \text{ FePO}_4 + 4 \text{ Fe}(OH)_3$ |
| 12 | Ε | At the negative electrode, the strongest oxidizing agent reacts first, that is Cu ²⁺ . |
| | | At the positive electrode, the strongest reducing agent reacts first, that is Br |
| 13 | Α | $\Delta G_{\text{total}} = \Delta G_1 + \Delta G_2 \text{ or}$ |
| | | $-4 \times F \times \Delta E = -2 \times F \times 1.468 + \{-2 \times F \times (-0.126)\}, \text{ thus}$ |
| | | $\Delta E = \frac{-1.468 + 0.126}{-2} = 0.671 \text{ V} \cdot$ |

Analysis

| 14 | С | When the peak area of 85A in chromatogram B is equal to that in chromatogram A, the peak area of vitamin E in chromatogram B is $\frac{12.717}{12.600} \times 7.902 = 7.975.$ The concentration of vitamin E in blueberry juice is $\frac{7.975}{7.617} \times 4.50 \cdot 10^{-4} = 4.71 \cdot 10^{-4} \text{ mol L}^{-1}.$ |
|----|---|---|
| 15 | D | The pH transition range of an indicator must fit on a steep part of the pH curve. |
| 16 | D | There is 0.1494 g H ₂ A in the titrated 25.00 mL. After the addition of 18.0 mL 0.100 M sodium hydroxide solution, all of the H ₂ A has been converted. Therefore $\frac{1}{2} \times 18.0 \times 0.100 \times 10^{-3}$ mol H ₂ A has reacted. The molar mass is therefore $\frac{0.1494}{\frac{1}{2} \times 18.0 \times 0.100 \times 10^{-3}} = 166 \text{ g mol}^{-1}$. |

Calculations and Green Chemistry

| 17 | С | Suppose x g of Mg reacts to form MgO and y g of Mg reacts to form Mg $_3$ N $_2$, |
|----|---|--|
| | | Then $\frac{x}{24.31}$ mol MgO is formed, which is $\frac{x}{24.31} \times 40.305 = 1.658x$ g MgO |
| | | and $\frac{1}{3} \times \frac{y}{24.31}$ mol Mg ₃ N ₂ , which is $\frac{1}{3} \times \frac{y}{24.31} \times 101.0 = 1.385y$ g Mg ₃ N ₂ . |
| | | This produces the following system of two equations with two variables: |
| | | x + y = 1.000 and |
| | | 1.658x + 1.385y = 1.584 |
| | | Solving this gives $y = 0.27$. |
| | | The mass percentage of Mg ₃ N ₂ is $\frac{0.27 \times 1.385}{1.584} \times 100\% = 24\%$. |
| 18 | D | $E - \text{factor} = \frac{\text{total mass of all reactants} - \text{mass of desired product}}{\text{total mass of all reactants}} =$ |
| | | mass of desired product |
| | | $\frac{181.88 + 5 \times 40.08 - 0.85 \times 101.88}{100.85 \times 100.88} = 3.4$ |
| | | 0.85×101.88 |

Thermochemistry

| 19 | С | A catalyst lowers the activation energy and does not influence the reaction enthalpy. |
|----|---|---|
| 20 | | The reaction enthalpy is given by $ \Delta H_r = -\Delta H_f(\text{CuSO}_4(s)) - 5 \times \Delta H_f(\text{H}_2\text{O}(l)) + \Delta H_f(\text{CuSO}_4.5\text{H}_2\text{O}(s)) \\ = -(-7.71 \cdot 10^5) - 5 \times (-2.86 \cdot 10^5) + (-22.78 \cdot 10^5) = -0.77 \cdot 10^5 \text{ J per 5 mol H}_2\text{O}. $ That is $ \frac{-0.77 \cdot 10^5}{5} = -0.154 \cdot 10^5 \text{ J per mol H}_2\text{O or } -15.4 \text{ kJ mol}^{-1}. $ |

Problem 1 The decomposition of dinitrogen pentoxide

(21 points)

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□1 Maximum score 8

An example of a correct answer is:

$$\Delta H_c = -11.3 + 2 \times 33.2 = +55.1 \text{ kJ mol}^{-1}$$

$$\Delta S_r = -355.6 + 2 \times 240 + \frac{1}{2} \times 205 = +227 \text{ J mol}^{-1} \text{ K}^{-1}$$

Thus
$$\Delta G_r = \Delta H_r - T \Delta S_r = 55.1 \times 10^3 - 323 \times 227 = -1.82 \cdot 10^4 \text{ J mol}^{-1}$$

It is also true that
$$\Delta G_r = -RT \ln K$$
, thus $K = e^{-\frac{\Delta G}{RT}} = e^{-\frac{-1.82.10^4}{8.314 \times 323}} = 8.78 \cdot 10^2$.

That is very large, so the equilibrium lies far to the right and the reaction can be considered as to proceed to completion.

- · in the calculation of ΔH_r , the formation enthalpy of N_2O_5 with a negative sign 1
- · in the calculation of ΔH_r , 2 × formation enthalpy of NO₂ with a positive sign
- · correct summation of the formation enthalpies
- · in the calculation of ΔS_r , the absolute entropy of N_2O_5 with a negative sign
- · in the calculation of ΔS_r , 2 × the absolute entropy of NO₂ and $\frac{1}{2}$ × the absolute entropy of O₂ with a positive sign
- · correct summation of the absolute entropies
- · calculation of ΔG_r
- · calculation of K, and noting that it is very large (meaning the equilibrium lies far to the right)
- 2 Maximum score 1

Since the oxygen escapes, the reverse reaction cannot take place.

□3 Maximum score 4

An example of a correct answer is:

At completion,
$$\frac{1.01 \cdot 10^5 \times V_{\infty} \times 10^{-6}}{8.314 \times 303} = 4.01 \cdot 10^{-5} \times V_{\infty}$$
 mol O₂ is formed.

There was initially $2 \times 4.01 \cdot 10^{-5} \times V_{\infty}$ mol N_2O_5 present in 0.100 L solution, thus

$$[N_2O_5]_0 = \ \frac{2\times 4.01\cdot 10^{-5}\times \textit{V}_{_{\infty}}}{0.100} = 8.02\cdot 10^{-4}\times \textit{V}_{_{\infty}} \ \ \text{mol L}^{-1}.$$

At time t, V_t cm³ of O_2 has formed, so $8.02 \times 10^{-4} \times V_t$ moles of N_2O_5 per litre have been converted.

Thus
$$[N_2O_5]_t = 8.02 \cdot 10^{-4} \times V_{\infty} - 8.02 \cdot 10^{-4} \times V_t = (V_{\infty} - V_t) \times 8.02 \cdot 10^{-4} \text{ mol L}^{-1}$$
, thus $F = 8.02 \cdot 10^{-4}$.

- · correct conversion from cm³ to m³ and °C to K
- · calculation of the number of moles of O_2 in V_{∞} cm³ and V_t cm³ respectively
- · calculation of the number of moles of N_2O_5 initially present and the number of moles of N_2O_5 converted in t sec
- · calculation of the decrease of $[N_2O_5]$ in t sec and of F

4 Maximum score 4

An example of a correct answer is:

At t = 0 s, $[N_2O_5]$ is equal to $6.80 \cdot 10^{-2}$ mol L⁻¹, at $t = 8.5 \cdot 10^3$ s, $[N_2O_5]$ has decreased to $3.40 \cdot 10^{-2}$ mol L⁻¹ and again $8.5 \cdot 10^3$ s later, at $t = 17 \cdot 10^3$ s, to $1.70 \cdot 10^{-2}$ mol L⁻¹.

The half-life is therefore $8.5 \cdot 10^3$ s and is independent of concentration, which is the case for a first order reaction.

- · choice of (at least) two concentrations that differ by a factor of 2
- reading the corresponding times
- · calculation of the half-life
- · observation that the half-life is independent of concentration (so it is a first order reaction)

□5 Maximum score 2

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{8.5 \cdot 10^3} = 8.2 \cdot 10^{-5} \text{ s}^{-1}$$

 \cdot calculation of k

Note

If an incorrect answer to question 5 is the consequential result of an incorrect answer to question 4, mark the answer to question 5 as correct.

□6 Maximum score 2

An example of a correct answer is:

For this first order reaction we have $\ln \frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$. Substituting $[N_2O_5]_0 = V_\infty \times F$ and

$$[N_2O_5]_t = (V_{\infty} - V_t) \times F$$
 gives $\ln \frac{V_{\infty} \times F}{(V_{\infty} - V_t) \times F} = \ln \frac{V_{\infty}}{(V_{\infty} - V_t)} = kt$.

So if you plot $\ln \frac{V_{_{\infty}}}{(V_{_{\infty}}-V_{_t})}$ versus time in a diagram, you get a straight line. The slope of this

line is k.

· demonstrate that
$$\frac{[N_2O_5]_0}{[N_2O_5]_t} = \frac{V_{\infty}}{(V_{\infty} - V_t)}$$

· rest of the answer

1

□7 Maximum score 1

An example of a correct answer is:

□8 Maximum score 7

An example of a correct answer is:

+
$$Cl_2$$
 + HCl
 Cl
 NO_2
 Cl
 NO_2
 NH_2
 Cl
 NH_2
 Cl
 NH_2
 Cl
 Cl

in the first equation correct formulas before the arrow
in the first equation correct formulas after the arrow
in the second equation correct formulas before the arrow
in the second equation correct formulas after the arrow
in the third equation correct formulas before the arrow
in the third equation correct formulas after the arrow
correct coefficients in the third equation

Note

When HCl and/or HNO₃ are written as $H^+ + Cl^-$ and $H^+ + NO_3^-$ respectively, mark this as correct.

□9 Maximum score 3

An example of a correct answer is:

A synthesis route that starts with the nitration of benzene is possible. After the nitration, the nitro group must first be converted into an amino group, followed by chlorination, and then the chlorine atom is replaced by an OH group.

- · (a synthesis route that starts with the nitration of benzene is possibe) after nitration, the nitro group must be converted into an amino group
- · followed by chlorination
- then replacement of Cl with OH

If an answer is given as: "It is not possible because the nitro group is a meta-directing group, and therefore, chlorination will (mainly) result in *meta*-chloronitrobenzene".

□10 Maximum score 3

An example of a correct answer is:

- · the structural formula of *para*-chloronitrobenzene and OH⁻ before the arrow and the structural formulas of the nitrobenzyne, Cl⁻ and H₂O after the arrow
- · all charges and relevant electron pairs correctly represented
- · the curly arrows correctly represented

□11 Maximum score 1

An example of a correct answer is:

1

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2

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□12 Maximum score 4

An example of a correct calculation is:

The yield of the total conversion of benzene to paracetamol is

 $0.90 \times 0.92 \times 0.65 \times 0.48 \times 0.85 = 0.22$.

That means that per Mmol benzene ultimately 0.22 Mmol paracetamol can be formed.

1.00 ton benzene is
$$\frac{1.00}{78.11}$$
 Mmol, thus, from that $0.22 \times \frac{1.00}{78.11}$ Mmol paracetamol can be

formed, that is $0.22 \times \frac{1.00}{78.11} \times 151.17 = 0.43$ ton paracetamol.

- · calculation of the yield of the total conversion of benzene to paracetamol 1
- · calculation of the number of Mmoles of benzene in 1.00 ton of benzene
- · calculation of the number of Mmoles of paracetamol that can be formed from this
- · calculation of the number of tons of paracetamol that can be formed

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□13 Maximum score 3

Examples of a correct calculation are:

Suppose that wüstite contains p mol Fe²⁺ and q mol Fe³⁺ per mol O²⁻, then it follows that: p + q = 0.87 and 2p + 3q = 2.

Solving this system of two equations with two unknowns results in p = 0.61 and q = 0.26. Thus p : q = 2.3 : 1.0.

- · formulation of the equation p + q = 0.87
- · formulation of the equation 2p + 3q = 2
- · rest of the calculation

and

The average charge of the iron ions is $\frac{2}{0.87}$ = +2.3. Suppose there are p moles Fe²⁺ in one

mol of iron ions with an average charge of +2.3, then there are (1-p) moles Fe³⁺, and the following equation applies 2p + 3(1-p) = 2.3. This results in p = 0.7.

Thus per mol of iron ions, there is 0.7 mol Fe^{2+} and 0.3 mol Fe^{3+} .

Thus the molar ratio Fe^{2+} : $Fe^{3+} = 0.7 : 0.3 = 2.3 : 1.0$.

- · calculation of the average charge of the iron ions
- · (supposing that there are p moles of Fe²⁺ per mol of iron ions) notion that 2p + 3(1-p) = 2.3
- · rest of the calculation

□14 maximum score 1

Examples of a correct answer are:

- If all positions of positive ions in the lattice were occupied by Fe²⁺ and Fe³⁺ ions, the substance would not be neutral.
- If two Fe³⁺ ions are present in the lattice, one Fe²⁺ ion must be missing.

□15 Maximum score 6

An example of a correct answer is:

The volume of the unit cell is $(2 \times 214)^3 = 7.84 \cdot 10^7 \text{ pm}^3 \text{ or } 7.84 \cdot 10^{-29} \text{ m}^3$.

The unit cell contains 4 oxide ions and (on average) 4x iron ions.

The (average) mass of the unit cell is thus $4 \times 16.00 + 4x \times 55.85$ u, or

 $(4 \times 16.00 + 4x \times 55.85) \times 1.66 \cdot 10^{-27}$ kg.

Thus, for the density applies $\frac{(4 \times 16.00 + 4x \times 55.85) \times 1.66 \cdot 10^{-27}}{7.84 \cdot 10^{-29}} = 5.71 \cdot 10^{3} \text{ kg m}^{-3}.$

From this it follows that x = 0.92.

- · notion that the edge length of the unit cell is 2×214 pm
- · calculation of the volume of the unit cell
- · notion that the unit cell contains 4 oxide ions and (on average) 4x iron ions
- · calculation of the mass of the unit cell
- · dividing the calculated mass of the unit cell by the calculated volume of the unit cell and equating this to the given density
- \cdot calculation of x

□16 Maximum score 8

Examples of a correct calculation are:

26.41 mL 0.0200 M potassium permanganate solution contains 26.41 \times 0.0200 mmol MnO₄⁻. This has reacted with $5 \times 26.41 \times 0.0200 = 2.64$ mmol Fe²⁺.

Because Fe_xO can be interpreted as a mixture of FeO and Fe_2O_3 , the 250 mg Fe_xO must have contained 2.64 mmol FeO and this is $2.64 \times 71.844 = 190$ mg FeO.

Then it contained 250 – 190 = 60 mg Fe₂O₃ and this contains $2 \times \frac{60}{159.69} = 0.75$ mmol Fe³⁺.

Thus, 250 mg Fe_xO contained 2.64 + 0.75 = 3.39 mmol iron ions and

$$2.64 + \frac{3}{2} \times 0.75 = 3.77$$
 mmol oxide ions.

Thus, the formula of the examined wüstite is $Fe_{3.39}O_{3.77}$ or $Fe_{0.90}O$. Thus, x = 0.90.

 $\begin{array}{c} \cdot \text{calculation of the number of mmoles of } \text{MnO}_4^- \text{ used for the titration} & 1 \\ \cdot \text{calculation of the number of mmoles of } \text{Fe}^{2+} \text{ that reacted with this} & 1 \\ \cdot \text{calculation of the number of mg of Fe0 that the 250 mg Fe}_x\text{O contained} & 1 \\ \cdot \text{calculation of the number of mg of Fe}_2\text{O}_3 \text{ that the 250 mg Fe}_x\text{O contained} & 1 \\ \cdot \text{calculation of the number of mmoles of Fe}^{3+} \text{ that the 250 mg Fe}_x\text{O contained} & 1 \\ \cdot \text{calculation of the total number of mmoles of iron ions in the 250 mg Fe}_x\text{O} & 1 \\ \cdot \text{calculation of the total number of oxide ions in the 250 mg Fe}_x\text{O} & 1 \\ \cdot \text{calculation of } x & 1 \\ \end{array}$

and

26.41 mL 0.0200 M potassium permanganate solution contains 26.41 \times 0.0200 mmol MnO₄⁻. This has reacted with $5 \times 26.41 \times 0.0200 = 2.64$ mmol Fe²⁺.

Thus, the 250 mg Fe_xO contained $2.64 \times 55.85 = 147$ mg Fe²⁺

and in total $250 - 147 = 103 \text{ mg Fe}^{3+}$ and 0^{2-} .

Suppose it contains p mmol Fe³⁺ and q mmol O²⁻ than the following applies

55.85p + 16.00q = 103 (equation 1).

Because the substance is electrically neutral, the following also applies

$$3p - 2q + 2 \times 2.64 = 0$$
 (equation 2).

Solving this system of two equations with two unknowns results in p = 0.76 and q = 3.78. Thus, the 250 mg Fe_xO contained 2.64 + 0.76 = 3.40 mmol iron ions and 3.78 mmol oxide

ions. Thus, the formula of the examined wüstite is $Fe_{3.39}O_{3.77}$ or $Fe_{0.90}O$.

Thus, x = 0.90.

· calculation of the number of mmoles of MnO₄ used for the titration 1 · calculation of the number of mmoles of Fe2+ that reacted with this · calculation of the number of mg of Fe²⁺ in the 250 mg Fe_xO and of the total number of mg of Fe^{3+} and O^{2-} in the 250 mg Fe_xO 1 · formulating equation 1 1 · formulating equation 2 1 · solving the system of equations 1 · calculation of the total number of mmoles of iron ions in the 250 mg Fe_xO 1 · rest of the calculation 1