44th National Chemistry Olympiad

University Leiden

THEORY TEST

QUESTION BOOKLET

Monday 12 June 2023

- This test is composed of 7 problems with 39 open questions and an answer booklet.
- Use a separate answer sheet for each problem, making sure to include your name on each sheet. Maintain a 2 cm margin on all sides of the page.
- The maximum score for this test is 120 points.
- The test will last a maximum of 4 clock hours.
- Required resources: (graphic) calculator and Binas 6th edition or Sciencedata 1st print.
- Each question includes the number of points that a correct answer to that question will earn.

Problem 1 Lithium-ion battery   (13 points)

In 2019, John B. Goodenough, M. Stanley Whittingham and A. Yoshino were awarded the Nobel Prize in chemistry for the development of the lithium-ion battery. A lithium-ion battery consists of a copper electrode covered with a layer of graphite containing lithium, represented by LiC_6, and an aluminum electrode covered with a layer of $LiCoO_2$. The equations for the half-reactions on which the operation of the cell relies, can be shown as follows, including the corresponding standard electrode potentials under standard conditions:

$$Li^+ + C_6 + e^- \rightleftharpoons LiC_6, \text{ with } V^0 = -3.05 \text{ V}$$

and

$$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2, \text{ with } V^0 = +1.00 \text{ V}$$

▫1   Write down the equation of the complete reaction when a lithium-ion battery provides a current.   2

▫2   Calculate the cell potential of a fully charged battery under standard conditions.   1

▫3   Give the charges of the particles in the CoO_2 and the $LiCoO_2$. Indicate these charges in the sentences on the answer sheet.   3

An important characteristic of a battery is its capacity. This is measured in mAh.

▫4   Calculate the minimum amount of lithium in g that is required to be present in a lithium-ion battery to deliver a current of 200 mA over 2 days.   3

Based on the same principle of the lithium-ion battery, it should be possible to make a battery using magnesium instead.

We compare such a magnesium-ion battery with a lithium-ion battery. When fully charged, there are equal amounts in gram of the metal in both batteries. We allow both batteries to provide the same constant current until they are fully discharged.

▫5   Explain which battery is able to provide power for the longest period of time and calculate the mathematical ratio between the times of the two different batteries (to full discharge).   4
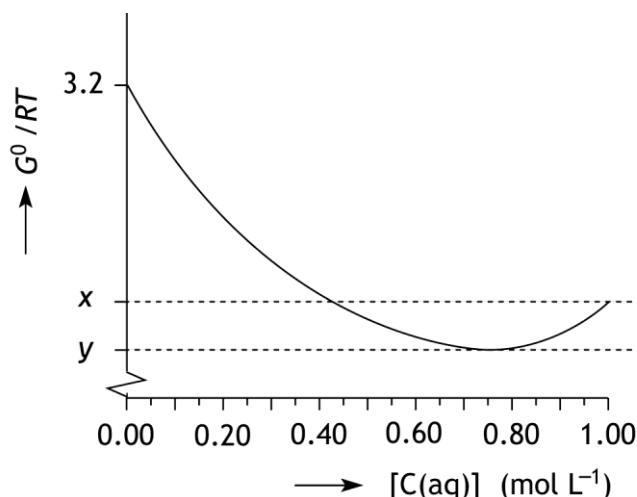
Problem 2 *G* and *K* (13 points)

Consider the following general chemical reaction in aqueous environment:

A(aq) + B(aq) $\rightleftharpoons$ C(aq) + D(aq)
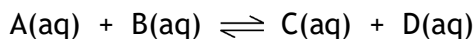
A 1.00 liter solution containing 1.00 mol of substances A and B is prepared and the reaction is allowed to take place. The change in Gibbs free energy, G^0 (in units RT), of the system versus the concentration of C at 298 K is as follows:

With use of the diagram, the equilibrium constant K, at 298 K, can be calculated.

▫6   Calculate the equilibrium constant at 298K.   4

▫7   Calculate $\Delta_r G^0$ in $J\,mol^{-1}$. (The answer to question 6 is required. If you do not have an answer for question 6, use K = 12 – this is not the correct answer for question 6.)   2

▫8   Explain which values are represented by *x* and *y* on the vertical axes.   4

Another 1.00 mol of B is added to the solution at equilibrium. The temperature and the volume of the solution remain unaffected.

▫9   Comment on the values of [A], [B], [C] and [D] once equilibrium is re-established, when compared to the values of [A],[B], [C] and [D] in the initial equilibrium.
Give your answer on the answer sheet by circling your choice from 'larger than', 'equal to', and 'smaller than'.   3

Problem 3 Sulfuryl chloride   (12 points)

Sulfurylchloride is a compound consisting of sulfur, chlorine and oxygen. The molecular formula is SO_2Cl_2.

The Lewis structure of sulfuryl chloride can be seen below:

$$
\overline{\underline{Cl}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\overline{\underline{Cl}}
$$
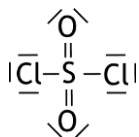
During the formation of the bonds within the molecule, the following excited state of the sulfur atom can be assumed: $3s^1$, $3p^3$, $3d^2$.

□10 Give a description of a sulfuryl chloride molecule. Pay attention to the following:
  – the shape of the molecule;
  – the type of hybridization of the sulfur atom and the oxygen atom;
  – the type of bonds in the molecule: π-bonds ,σ-bonds; also describe how these bonds were formed.   6

Sulfuryl chloride decomposes readily at higher temperatures, leading to the formation of sulfur dioxide and chlorine. The following equilibrium is reached:

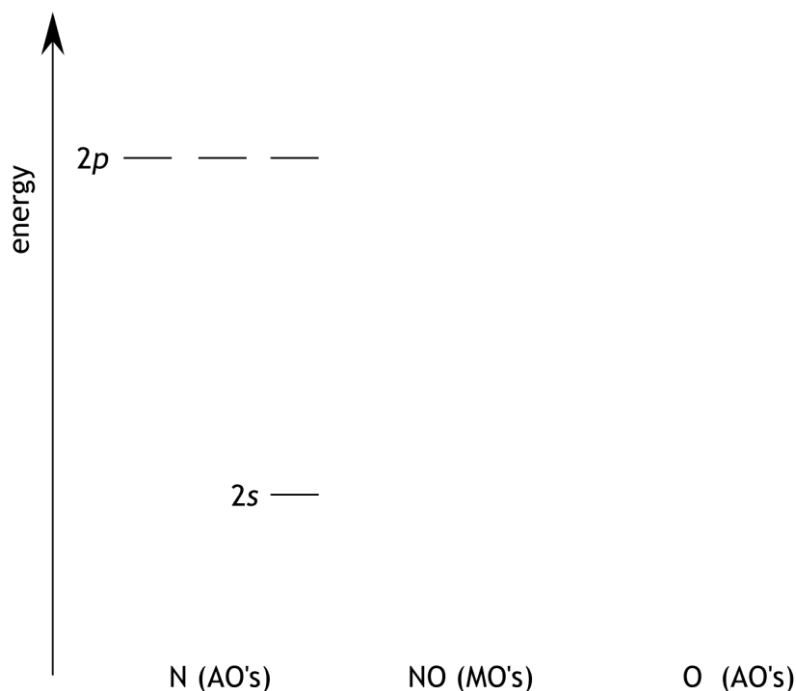$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$
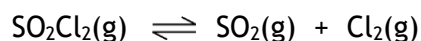
When 1.95 g of sulfuryl chloride is heated to 157 °C, the total volume of gas at equilibrium is 1.00 dm^3 and $p = p_0$.

□11 Calculate the value of K_p for the equilibrium established at 157 °C.   6

Problem 4 NO   (24 points)
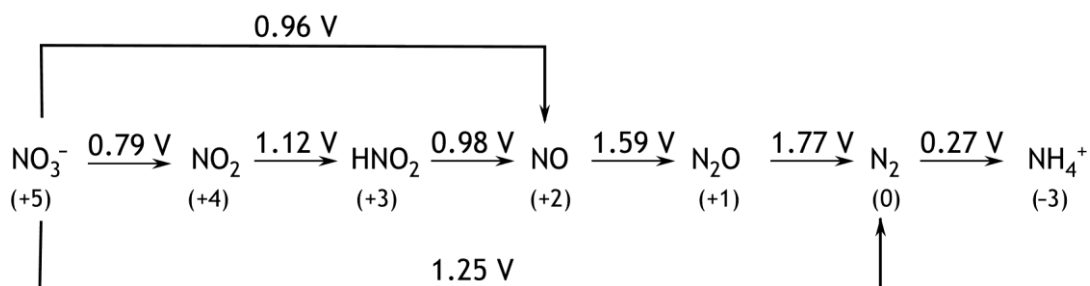
Below is the start for a MO diagram of nitrogen monoxide. The $2s$ and $2p$ levels of the nitrogen atom are already indicated in the diagram.

The above diagram is also present in the answer sheets of this test.

◻12 Draw the following on the diagram provided in the answer sheets:
  - the $2s$ and $2p$ levels of the oxygen atom;
  - the molecular orbitals of the nitrogen monoxide molecule, including the common designations for 'bonding' and 'anti-bonding';
  - fill the atomic and molecular orbitals with electrons according to the Aufbau principle.   6

◻13 Calculate the bond order of the NO molecule.   2

The strength of the bond between the N atom and the O atom in a nitrogen monoxide molecule can be calculated using the enthalpy of reaction of the reaction between NO(g) and H_2(g), whereby N_2(g) and H_2O(g) are formed.

◻14 Calculate the enthalpy of reaction of the reaction between NO(g) and H_2(g) whereby N_2(g) and H_2O(g) are formed.   3

◻15 Calculate the bond energy, in J mol^{-1}, of the bond between N and O in NO.   3

From a thermodynamic perspective, NO is an unstable compound at 298K. This can be concluded from the Latimer diagram of nitrogen, which is provided below. The conditions for the conversions shown in the diagram are 298 K, $p = p_0$ and pH = 0.00 ([H^+] = 1.0 M).

$$\overset{0.96\ V}{\underset{}{\text{NO}_3^-}}$$

NO$_3^-$ $\xrightarrow{0.79\ V}$ NO$_2$ $\xrightarrow{1.12\ V}$ HNO$_2$ $\xrightarrow{0.98\ V}$ NO $\xrightarrow{1.59\ V}$ N$_2$O $\xrightarrow{1.77\ V}$ N$_2$ $\xrightarrow{0.27\ V}$ NH$_4^+$

(+5)   (+4)   (+3)   (+2)   (+1)   (0)   (-3)

0.96 V (from NO$_3^-$ to NO)

1.25 V (from NO$_3^-$ to N$_2$)

In an aqueous solution at pH = 0.00, NO could be converted to HNO$_2$ and N$_2$O during a so-called auto redox reaction.

▫16   Give the equation for this reaction.   3

▫17   Calculate the equilibrium constant for this reaction. Use, among other things, the fact that for a redox reaction the change in free energy can be expressed as $\Delta G^0 = -nF\Delta V^0$.   4

For each conversion in the above Latimer diagram it holds that $\Delta G^0 = -nFV^0$.
Using this relationship and data from the Latimer diagram above, the V^0 for the conversion of NO to NH$_4^+$ can be calculated as follows: $\dfrac{1.59 + 1.77 + 3 \times 0.27}{5}$.

▫18   Derive this relationship.   3

# Problem 5 Crazy scents   (27 points)

The structural formulas of fragrances found in plants are represented in the diagram below. They are widely applied, for example in the perfume industry.

1   **2**   **3**   **4**   **5**
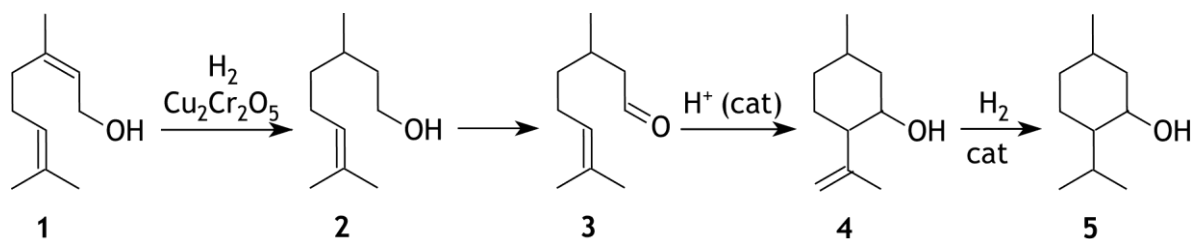
These are nerol (**1**), citronellol (**2**), citronellal (**3**), isopulegol (**4**) and menthol (**5**). Isolating these compounds from plants is not always a simple process. Moreover, the quantities obtained are often insufficient. It is for this reason that synthetic conversions are also used during the production of these fragrances. These are also indicated in the diagram above.

▫19 Give the systematic name of nerol (**1**); make use of *E*/*Z* notation.   3

▫20 Use the diagram to determine if the conversion from **1** to **2** is chemo selective.   2

▫21 Use the diagram to determine if the conversion from **1** to **2** is stereo selective.   2

▫22 Which reagent(s) is/are suitable for the conversion from **2** to **3**?
     Choose from the following reagents:
     a. CrO_3, pyridine
     b. H_2 (Pd/C)
     c. $LiAlH_4$
     d. $Na_2Cr_2O_7$, H^+, H_2O
     e. O_3
     f.   PCC (pyridinium chlorochromate)   4

After the reaction that leads to the conversion of 2 to 3 is completed, the IR-spectrum is recorded for the product of the reaction. A section of that IR-spectrum is shown below. A section of the IR-spectrum for **2** is also shown.

IR-spectrum of **2**   IR-spectrum of the reaction product
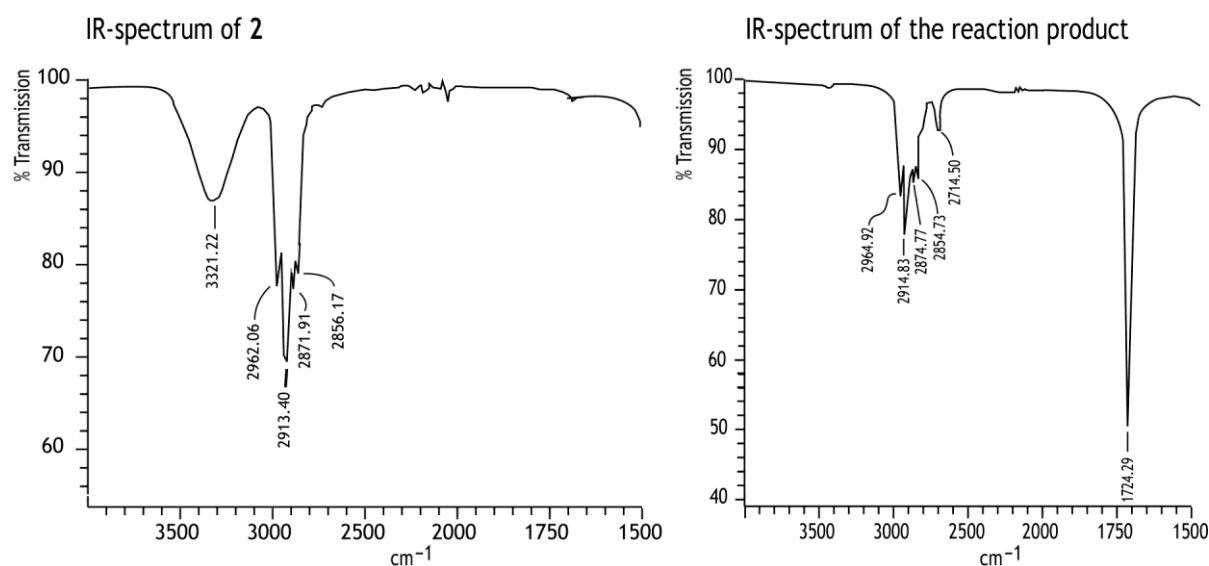
From these IR-spectra, arguments that support the conversion from **2** to **3** can be derived.

◻23   Give two of these arguments and clarify how they support the desired conversion.   2

For the structural formula drawn for isopulegol (**4**), multiple stereo-isomers are possible.

◻24   Explain how many stereo-isomers in total are possible for the structural formula that is
drawn for isopulegol.   2

In the molecules of menthol (**5**), the three side chains in the cyclohexane ring are in the
equatorial position.
The chair conformation of the cyclohexane ring is drawn in the answer sheets.

◻25   In the answer sheets, draw the 3D structure of a molecule of menthol.
Make use of the cyclohexane ring that is already drawn. Draw the three side groups in the
equatorial position.   3

The synthesis of **4** from **3** can be carried out under the influence of H^+ (acidic solution) as
catalyst. The ring closure that takes place can be thought of as an electrophilic addition
reaction to a $C = C$ bond, followed by an E1-elimination reaction.
The mechanism takes place according to the following steps:
-    protonation of the carbonyl group;
-    electrophilic addition to the $C = C$ bond, where an intermediate carbocation is
     produced;
-    elimination of H^+ leading to the product.

The structure of citronellal (**3**) is provided in the answer sheets.

◻26   Show the mechanism for the synthesis of **4** from **3** in the answer sheets.
-    start with the structure of **3** that is already provided;
-    when representing the mechanism, use similar structures to those already given;
-    include the non-bonding electron pairs;
-    make use of curly arrows to indicate how electron pairs move when forming and
     breaking bonds;
-    include all formal charges in the appropriate places.   6

Three ^{1}H-NMR-spectra (in the area above 2.5 ppm) are provided in the answer sheets.
These are spectra from the three compounds from series **1** – **5**. The conditions under which
these spectra were recorded are identical (solvent $CDCl_3$, 300 MHz).

◻27   Write the number of the corresponding compound in each spectrum in your answer sheets.   3

Problem 6 Synthesis of Oseltamivir   (14 points)

Oseltamivir is a registered medicine (Tamiflu®) that is used to treat the influenza virus. Due to the importance of this medicine, multiple pathways for the synthesis of Oseltamivir have been developed. The first part of one of these pathways is provided below and begins with shikimic acid (**1**), **that is** isolated from star anise.
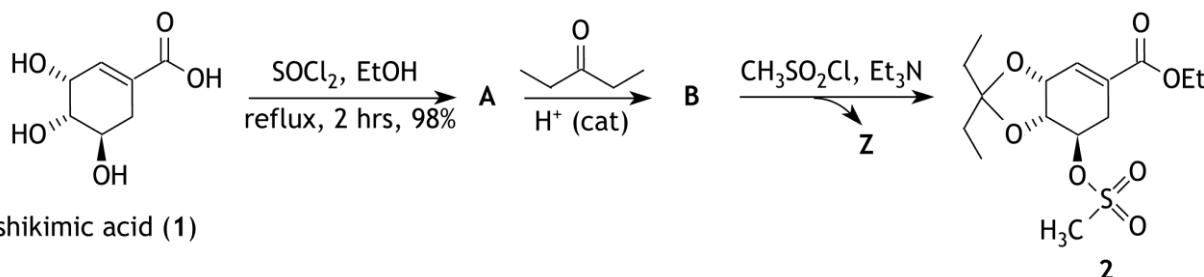
shikimic acid (**1**)

During the conversion of shikimic acid (**1**) to compound **A**, ethanol is both reagent and solvent. A limited amount of thionyl chloride ($SOCl_2$) is gradually added to a mixture of ethanol and shikimic acid.
The reaction between ethanol and thionyl chloride produces hydrogen chloride, which acts as a catalyst in the formation of **A** from shikimic acid and ethanol.
Then **A** reacts with pentane-3-one under the influence of an acid catalyst to form compound **B**.
Finally, CH_3SO_2Cl is used to prepare compound **2** in the presence of triethylamine.

The reaction of ethanol with thionyl chloride produces two other compounds other than hydrogen chloride.

◻28   Give the formulas of these two compounds.   2

A procedure for the conversion of shikimic acid to **A** is described below:

In a 250 mL round-bottom flask, equipped with a reflux condenser and a magnetic stirrer, under an atmosphere of an inert gas, 19.90 g (= 0.114 mol) shikimic acid is suspended in 80 mL (= 1.4 mol) ethanol. To this mixture 4.16 mL (= 0.057 mol) thionyl chloride is added gradually over the course of 10 minutes. The mixture is refluxed for 2 hours, after which compound **A** is isolated with a 98% yield.

Due to the presence of OH groups in the shikimic acid molecule, thionyl chloride can react with ethanol as well as with shikimic acid. Whether that reaction affects the final yield of **A** depends on the type of OH groups in shikimic acid that react.

When the reaction takes place with the OH group of the COOH group, it has no influence on the yield of **A**.
When the reaction takes place with the alcoholic OH groups, it does have an influence on the yield of **A**.

◻29   Explain why the reaction between thionyl chloride with shikimic acid, via the OH of the
COOH group, has no influence on the yield of **A**.   2

□30 Explain that, for the reaction with thionyl chloride, it can be deduced from the data in the above description that the reactivity of the OH groups of ethanol is greater than the reactivity of the alcoholic OH groups of shikimic acid. 3

□31 Give the formula of **Z.** 2

□32 Explain, using the diagram, whether the reaction of **A** with pentan-3-one is regio selective. 2

□33 Explain whether the 'lower' C atom (to which the $-OSO_2CH_3$ group is attached) in the six-membered ring of compound **2** has the *R*- or *S*-configuration. Use a sketch in your explanation. 3

Problem 7 Oseltamivir determination   (17 points)

Oseltamivir is sold as the water-soluble salt of phosphoric acid, oseltamivir phosphate:
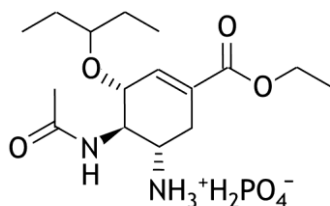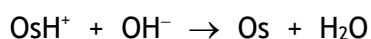

Oseltamivir phosphate

From here on, oseltimivir phosphate will be represented as $OsH^+H_2PO_4^-$.

In order to guarantee the quality of oseltamivir phosphate, the purity of the product must be checked regularly. This can be done, for example, by first converting the oseltamivir phosphate to oseltamivir chloride, OsH^+Cl^-. Excess caustic soda (a solution of NaOH) is added to a solution of this compound and finally a titration with hydrochloric acid is performed.

OsH^+Cl^- dissolves as follows:

$$OsH^+Cl^- \rightarrow OsH^+ + Cl^-$$
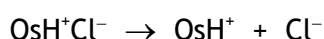
OsH^+ is a weak acid, with $pK_a = 7.90$. When caustic soda is added, the following reaction occurs:

$$OsH^+ + OH^- \rightarrow Os + H_2O$$

In such a determination, the oseltamivir phosphate from one 75.0 mg capsule is completely converted to oseltamivir chloride. This is dissolved in demineralized water and then the solution is filled to a final volume of 50.0 mL. Then 1,00 mL $5.00 \cdot 10^{-2}$ M caustic soda is added to 10.0 mL of this solution. The excess caustic soda is then back-titrated with $1.00 \cdot 10^{-3}$ M hydrochloric acid, of which 13.6 mL was required.

□34 Calculate the mass percentage of the oseltamivir phosphate in the capsule. Assume that the ester bond does not react during the addition of the caustic soda and the titration process.   6

Phenolphthalein is used as indicator during the back-titration.

□35 Would methyl orange also be a viable option to use, or would this result in a too high or too low result? Explain your answer.   3

To accurately determine the equivalence point of the titration, you could perform the titration and follow the absorbance A caused by the presence of phenolphthalein.

□36 Which of the following figures best indicates the progress of the absorbance during the titration? Explain your answer.   2
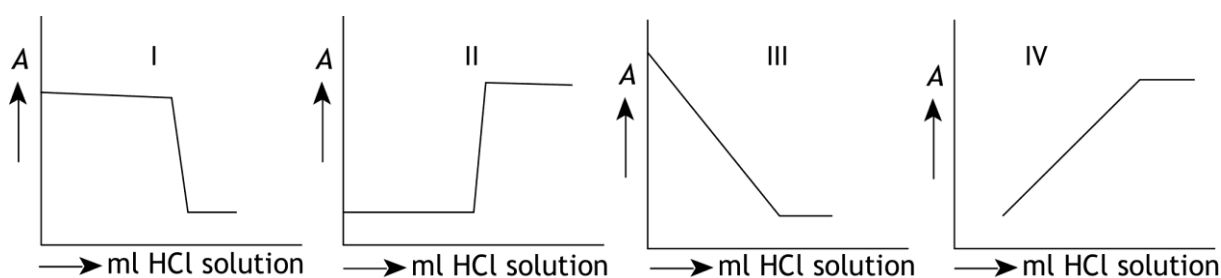
A titration curve for a solution of oseltamivir phosphate with caustic soda was established based on a pKa of 7.90 for the OsH^+ to investigate if the determination could also be carried out by dissolving the capsule containing the oseltamivir phosphate in water and titrating the solution directly.
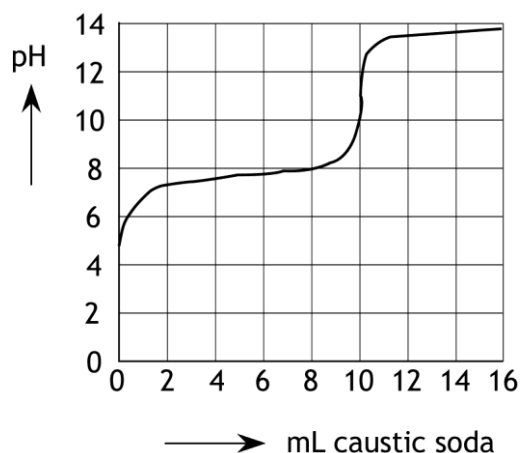
A peculiar aspect of this titration curve is that there is only one steep area, despite $OsH^+H_2PO_4^-$ being a triprotic acid.

▫37 Explain why there is only one steep area in the titration curve when oseltamivir phosphate is titrated with caustic soda, despite oseltamivir phosphate being a triprotic acid   2

The titration curve above shows that it is possible to titrate a solution of oseltamivir phosphate directly with caustic soda.

▫38 Using the titration curve above, explain that it is possible to titrate a solution of oseltamivir phosphate directly with caustic soda; also indicate which indicator you might use and give the color change of that indicator at the equivalence point.   3

▫39 Indicate the molar ratio for $OsH^+H_2PO_4^-$: OH^- during the direct titration of a solution of oseltamivir phosphate with caustic soda.   1