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UNIVERSITY OF RUHUNA – FACULTY OF ALLIED HEALTH SCIENCES
DEPARTMENT OF PHARMACY

THIRD BPHARM PART I EXAMINATION – JUNE 2022

PH 3113 ANALYTICAL CHEMISTRY -SEQ

TIME: TWO HOURS

INSTRUCTIONS

- There are **four** questions in parts **A**, **B** and **C** in this paper.
- Answer all the questions.
- No paper should be removed from the examination hall.
- Do not use any correction fluid.
- Use illustrations where necessary.

PART A

1.

1.1 Define the term "Reference Standard" (***10 marks***)

1.2 Briefly describe the uses of Reference Standards in the industry. (***20 marks***)

1.3 List four types of analytical procedures that need to be validated. (***10 marks***)

1.4 State the validation characteristics that you would consider for the validation of an Assay test. (***10 marks***)

1.5 Explain the term 'precision' in relation to analytical method validation. (***25 marks***)

1.6 A batch of aspirin manufactured was not pure. Analysis of a 121.2 g of the compound showed that only 109.2 g of it was aspirin. Calculate the percent purity of the product.

(***25 marks***)

PART B

2.

2.1 After supersaturation of a solution a precipitate formation has two stages.

2.1.1 What is meant by supersaturation and what are the two stages that follows? Explain briefly. (***15 marks***)

2.2 Six iron tablets containing $FeSO_4.7H_2O$ were dissolved in 100 cm^3 of 0.1 *mol* dm^{-3} HNO_3 with gentle heating. After cooling the solution to room temperature 2.5 cm^3 of 35 wt% NH_4OH was added to precipitate iron as $Fe_2O_3.xH_2O$. Then the precipitate was filtered and weighed as 0.344 g. This precipitate was ignited at a high temperature to give pure 0.309 g of Fe_2O_3 (FW=159.69 g/mol).

2.2.1 Calculate the amount of iron (AW= 55.845 g/mol) in all six tablets. (***20 marks***)

2.2.2 Report the average mg-Fe per tablet. (***10 marks***)

2.2.3 What is the purpose of adding conc. HNO_3 acid in the preparation of the initial solution?

(***05 marks***)

2.3 Define α_{y4-} in terms of the concentration of all forms of EDTA, [Y'] and write an expression for the pH dependent conditional formation constant of a metal-EDTA complex. (***10 marks***)

2.4 A 25.00-cm^3 aliquot of a solution containing Fe(III) and Al(III) was buffered to pH 2 and 2 cm^3 salicylic acid in methanol was added. The solution was titrated with 0.0200 *mol* dm^{-3} EDTA until the violet color of Fe(III)-salicylate complex just disappeared and required 14.80 cm^3. Then the pH of the solution was adjusted to 5 and 25.00 cm^3 of the same EDTA solution was added and boiled. After cooling to the room temperature, the solution was titrated with 0.0120 *mol* dm^{-3} Fe(III) solution until the first appearance of violet color and required 9.50 cm^3.

$\alpha_{y4-} = 2.6 \times 10^{-14}$ at pH 2 and 2.9×10^{-7} at pH 5. K_{fAlY} and K_{fFeY} are 1.3×10^{16} and 1×10^{25}, respectively.

2.4.1 What is the reason for boiling the solution prior to the second titration? (***05 marks***)

2.4.2 Calculate the conditional formation constant of both metal ions and comment on the pH at which one of the metal ions does not react significantly with EDTA. (***15 marks***)

2.4.3 Calculate the concentration of Fe (III) and Al (III)in the sample. (***20 marks***)

3.

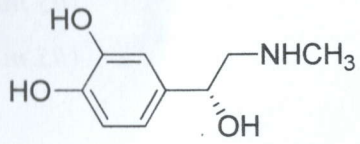
3.1 A 1.998 g sample containing Cl^- and ClO_4^- was dissolved in water to give a 250.00 cm^3 of solution. Argentometric titration of 25.00 cm^3 aliquot of this solution required 7.00 cm^3 of 0.1000 *mol* dm^{-3} $AgNO_3$ solution. A second 25.00 cm^3 aliquot of this solution was treated with $V_2(SO_4)_3$ following which titration required 20.00 cm^3 of the same $AgNO_3$ solution. Reaction with $V_2(SO_4)_3$ is as follows:

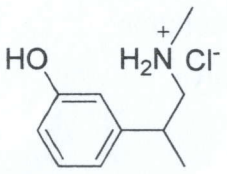
$$ClO_4^- + 4\ V_2(SO_4)_3 + 4\ H_2O \longrightarrow Cl^- + 12\ SO_4^{2-} + 8\ VO_2^+ + 8H^+$$

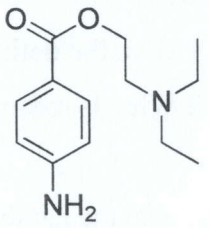
3.1.1 Calculate the percentage of Cl^- and ClO_4^- in the sample separately. (***30 marks***)

3.1.2 What indicator(s) would have been used in this titration? (***10 marks***)

3.2 Propose the most suitable titrimetric method for the assay each of the following drugs and briefly explain the principle of the titrimetric method that you proposed. (***30 marks***)







A-adrenaline (β-adrenoceptor agonist)

B-phenylephrine hydrochloride (decongestant)

C- procaine (local anesthetic)

3.3 A solution containing U(IV) in 0.5 *mol dm*$^{-3}$ H_2SO_4 was titrated potentiometrically with VO_2^+.

3.3.1 Calculate the E^0 for the complete titration reaction. (***10 marks***)

$$U^{4+} + 2\,VO_2^+ \longrightarrow UO_2^{2+} + 2\,VO^{2+}$$

3.3.2 Calculate the equivalence point potential of the titration. (***20 marks***)

E^0 for the two half- reactions involved in the titration are as follows:

$$VO_2^+ + 2\,H^+ + e \longrightarrow VO^{2+} + H_2O \qquad E^0 = 1.000\ V$$

$$UO_2^{2+} + 4\,H^+ + 2e \longrightarrow U^{4+} + 2\,H_2O \qquad E^0 = 0.334\ V$$

4.

4.1 An 11.0-g sample of vinegar was titrated with 0.5000 *mol dm*$^{-3}$ sodium hydroxide solution with phenolphthalein indicator giving the end point at 18.20 cm^3. Another sample of same vinegar with the same weight was titrated with methyl orange indicator and gave the end point at 4.50 cm^3.

4.1.1 Using a titration curve explain the use of correct indicator. (***20 marks***)

4.1.2 Calculate the purity of vinegar using the correct titration volume. (***30 marks***)

(Molecular weight and pK_a of acetic acid are 60.0 *g mol*$^{-1}$ and 4.8, respectively)

PART C

4.2 Buffers play an important role in the most of the enzyme catalyzed reactions.

4.2.1 Give the definition of a buffer solution. (***05 marks***)

4.2.2 What is meant by buffer capacity? (***05 marks***)

4.3 An enzyme catalyzed reaction, which is highly pH dependant, has shown its optimum rate at pH 6.5. Assume that you are planning to carry out this reaction at the optimum rate using one of the following acid/base pairs (**A-D**) as a buffer.

A-H_3PO_4/NaH_2PO_4 ($Ka_1 = 7.58 \times 10^{-3}$)

B-CH_3COOH/CH_3COONa ($Ka = 1.75 \times 10^{-5}$)

C-$H_2CO_3/NaHCO_3$ ($Ka_1 = 4.26 \times 10^{-7}$)

D-$H_3BO_3/Na_2B_4O_7$ ($Ka_1 = 5.75 \times 10^{-10}$)

Note: the acid dissociation constant of the weak acid in each pair is given in brackets.

4.3.1 Which acid/base pair would be suitable as a buffer to carry out the above reaction. (***05 marks***)

4.3.2 Give reason(s) for your choice. (***10 marks***)

4.3.3 Calculate the exact pH of the chosen buffer if the initial concentrations of the acid and its conjugate base are 0.0502 $mol\ dm^{-3}$ and 0.0538 $mol\ dm^{-3}$, respectively. (***10 marks***)

4.3.4 If you add 0.0100 *mol* of H_3O^+ into the 1.00 dm^3 of the above buffer solution, calculate the new pH of the buffer solution. Assume that the change of volume due to added H_3O^+ is negligible. (***15 marks***)

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