Analytical Chemistry

PROBLEM 4

A volume of 31.7 cm^3 of a 0.1-normal NaOH is required for the neutralization of 0.19 g of an organic acid whose vapour is thirty times as dense as gaseous hydrogen.

Problem:

4.1 Give the name and structural formula of the acid.

(The acid concerned is a common organic acid.)

SOLUTION

4.1

a) The supposed acid may be: HA, H_2A, H_3A, etc.

$$n(\text{NaOH}) = c\,V = 0.1 \text{ mol dm}^{-3} \times 0.0317 \text{ dm}^3 = 3.17 \times 10^{-3} \text{ mol}$$

$$n(\text{acid}) = \frac{3.17 \times 10^{-3}}{v} \text{ mol}$$

where v = 1, 2, 3,......

$$n(\text{acid}) = \frac{m(\text{acid})}{M(\text{acid})}$$

$$M(\text{acid}) = v \times \frac{0.19 \text{ g}}{3.17 \times 10^{-3} \text{ mol}} = v \times 60 \text{ g mol}^{-1} \qquad (1)$$

b) From the ideal gas law we can obtain:

$$\frac{\rho_1}{\rho_2} = \frac{M_1}{M_2}$$

$M(H_2)$ = 2 g mol^{-1}

M(acid) = 30 x 2 = 60 g mol^{-1}

By comparing with (1): $v = 1$

The acid concerned is a monoprotic acid and its molar mass is 60 g mol^{-1}.

The acid is acetic acid: CH_3–COOH

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THEORETICAL PROBLEMS

PROBLEM 1

An amount of 20 g of potassium sulphate was dissolved in 150 cm^3 of water. The solution was then electrolysed. After electrolysis, the content of potassium sulphate in the solution was 15 % by mass.

Problem:

What volumes of hydrogen and oxygen were obtained at a temperature of 20 °C and a pressure of 101 325 Pa?

SOLUTION

On electrolysis, only water is decomposed and the total amount of potassium sulphate in the electrolyte solution is constant. The mass of water in the solution:

1.1 Before electrolysis (on the assumption that ρ = 1 g cm^{-3}): $m(H_2O)$ = 150 g

1.2 After electrolysis:

$$m(H_2O) = m(\text{solution}) - m(K_2SO_4) = \frac{20\text{ g}}{0.15} - 20\text{ g} = 113.3\text{ g}$$

The mass of water decomposed on electrolysis:

$m(H_2O)$ = 150 – 113.3 = 36.7 g, i. e.

$n(H_2O)$ = 2.04 mol

Since, $2\,H_2O \rightarrow 2\,H_2 + O_2$

thus, $n(H_2)$ = 2.04 mol

$n(O_2)$ = 1.02 mol

$$V(H_2) = \frac{n(H_2)RT}{p} = \frac{2.04\ \text{mol} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times\ 293.15\ \text{K}}{101325\ \text{Pa}}$$

$\approx$ 0.049 m^3, resp. 49 dm^3

$V(O_2) = ½\ V(H_2) \approx 0.0245\ \text{m}^3 \approx 24.5\ \text{dm}^3$

PROBLEM 3

A 10 cm^3 sample of an unknown gaseous hydrocarbon was mixed with 70 cm^3 of oxygen and the mixture was set on fire by means of an electric spark. When the reaction was over and water vapours were liquefied, the final volume of gases decreased to 65 cm^3. This mixture then reacted with a potassium hydroxide solution and the volume of gases decreased to 45 cm^3.

Problem:

What is the molecular formula of the unknown hydrocarbon if volumes of gases were measured at standard temperature and pressure (STP) conditions?

SOLUTION

The unknown gaseous hydrocarbon has the general formula: C_xH_y

$$n(C_xH_y) = \frac{0.010 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = \frac{0.010}{22.4} \text{ mol}$$

Balance of oxygen:

- Before the reaction: 70 cm^3, i. e. $\frac{0.070}{22.4}$ mol
- After the reaction: 45 cm^3, i. e. $\frac{0.045}{22.4}$ mol

Consumed in the reaction: $\frac{0.025}{22.4}$ mol of O_2

According to the equation:

$$C_xH_y + (x + \frac{y}{4})\, O_2 = x\, CO_2 + \frac{y}{2}\, H_2O$$

Hence, $\frac{0.020}{22.4}$ mol of O_2 reacted with carbon and $\frac{0.020}{22.4}$ mol of CO_2 was formed ($C + O_2 = CO_2$),

$\frac{0.005}{22.4}$ mol O_2 combined with hydrogen and $\frac{0.010}{22.4}$ mol of water was obtained ($2\, H_2 + O_2 = 2\, H_2O$).

$3\ n(C) = n(CO_2) = \dfrac{0.020}{22.4}\ \text{mol}$

$n(H_2) = 2\ n(H_2O) = \dfrac{0.020}{22.4}\ \text{mol}$

$x : y = n(C) : n(H_2) = 0.020 : 0.020 = 1 : 1$

From the possible solutions C_2H_2, C_3H_3, C_4H_4, C_5H_5.only C_2H_2 satisfies to the conditions given in the task, i. e. the unknown hydrocarbon is acetylene.

PROBLEM 2

A sample of crystalline soda (**A**) with a mass of 1.287 g was allowed to react with an excess of hydrochloric acid and 100.8 cm^3 of a gas was liberated (measured at STP).

Another sample of different crystalline soda (**B**) with a mass of 0.715 g was decomposed by 50 cm^3 of 0.2 N sulphuric acid.

After total decomposition of soda, the excess of the sulphuric acid was neutralized which required 50 cm^3 of 0.1 N sodium hydroxide solution (by titration on methyl orange indicator).

Problems:

2.1 How many molecules of water in relation to one molecule of Na_2CO_3 are contained in the first sample of soda?

2.2 Have both samples of soda the same composition?

Relative atomic masses: $A_r(Na) = 23$; $A_r(H) = 1$; $A_r(C) = 12$; $A_r(O) = 16$.

SOLUTION

2.1 Sample **A**: $Na_2CO_3 . x H_2O$

$m(A) = 1.287$ g

$$n(CO_2) = \frac{p\,V}{R\,T} = 0.0045 \text{ mol} = n(A)$$

$$M(A) = \frac{1.287 \text{ g}}{0.0045 \text{ mol}} = 286 \text{ g mol}^{-1}$$

$M(A) = M(Na_2CO_3) + x\ M(H_2O)$

$$x = \frac{M(A) - M(Na_2CO_3)}{M(H_2O)} = \frac{(286 - 106) \text{ g mol}^{-1}}{18 \text{ g mol}^{-1}} = 10$$

Sample **A**: $Na_2CO_3 .10 H_2O$

2.2 Sample **B**: $Na_2CO_3 . x H_2O$

$m(B) = 0.715$ g

$H_2SO_4 + 2 NaOH = Na_2SO_4 + 2 H_2O$

$n(NaOH) = c V = 0.1 \text{ mol dm}^{-3} \times 0.05 \text{ dm}^3 = 0.005 \text{ mol}$

Excess of H_2SO_4: $n(H_2SO_4) = 0.0025$ mol

Amount of substance combined with sample **B**:

$n(H_2SO_4) = 0.0025 \text{ mol} = n(B)$

$$M(B) = \frac{0.715 \text{ g}}{0.0025 \text{ g mol}^{-1}} = 286 \text{ g mol}^{-1}$$

Sample **B**: $Na_2CO_3 .10 H_2O$

PROBLEM 4

An alloy consists of rubidium and one of the other alkali metals. A sample of 4.6 g of the alloy when allowed to react with water, liberates 2.241 dm^3 of hydrogen at STP.

Problems:

4.1 Which alkali metal is the component of the alloy?

4.2 What composition in % by mass has the alloy?

Relative atomic masses:

A_r(Li) = 7; A_r(Na) = 23; A_r(K) = 39; A_r(Rb) = 85.5; A_r(Cs) = 133

SOLUTION

4.1 M - alkali metal

Reaction: $2\,M + 2\,H_2O \rightarrow 2\,MOH + H_2$

$n(H_2) = 0.1$ mol

$n(M) = 0.2$ mol

Mean molar mass:

$$M = \frac{4.6\text{ g}}{0.2\text{ mol}} = 23\text{ g mol}^{-1}$$

4.2 Concerning the molar masses of alkali metals, only lithium can come into consideration, i.e. the alloy consists of rubidium and lithium.

$n(\text{Rb}) + n(\text{Li}) = 0.2$ mol

$m(\text{Rb}) + m(\text{Li}) = 4.6$ g

$n(\text{Rb})\,M(\text{Rb}) + n(\text{Li})\,M(\text{Li}) = 4.6$ g

$n(\text{Rb})\,M(\text{Rb}) + (0.2 - n(\text{Rb}))\,M(\text{Li}) = 4.6$

$n(\text{Rb})\,.\,85.5 + (0.2 - n(\text{Rb})) \times 7 = 4.6$

$n(\text{Rb}) = 0.0408$ mol

$n(\text{Li}) = 0.1592$ mol

$$\%\,\text{Rb} = \frac{0.0408\text{ mol} \times 85.5\text{ g mol}^{-1}}{4.6\text{ g}} \times 100 = 76$$

$$\% \text{ Li} = \frac{0.1592 \text{ mol} \times 7 \text{ g mol}^{-1}}{4.6 \text{ g}} \times 100 = 24$$

PROBLEM 3

A volume of 200 cm^3 of a 2-normal sodium chloride solution (ρ = 1.10 g cm^{-3}) was electrolysed at permanent stirring in an electrolytic cell with copper electrodes. Electrolysis was stopped when 22.4 dm^3 (at STP) of a gas were liberated at the cathode.

Problem:

3.1 Calculate the mass percentage of NaCl in the solution after electrolysis.

Relative atomic masses:

A_r(H) = 1; A_r(O) = 16; A_r(Na) = 23; A_r(Cl) = 35.5; A_r(Cu) = 64.

SOLUTION

3.1 Calculations are made on the assumption that the following reactions take place:

$2\ NaCl \rightarrow 2\ Na^+ + 2\ Cl^-$

cathode: $2\ Na^+ + 2\ e^- \rightarrow 2\ Na$

anode: $2\ Cl^- - 2\ e^- \rightarrow Cl^-$

$Cl_2 + Cu \rightarrow CuCl_2$

Because the electrolyte solution is permanently being stirred the following reaction comes into consideration:

$CuCl_2 + 2\ NaOH \rightarrow Cu(OH)_2 + 2\ NaCl$

On the assumption that all chlorine reacts with copper, the mass of NaCl in the electrolyte solution remains unchanged during the electrolysis.

$m(NaCl) = n\,M = c\,V\,M = 2\ mol\ dm^{-3} \times 0.2\ dm^3 \times 58.5\ g\ mol^{-1} = 23.4\ g$

$V(H_2) = 22.4\ dm^3$, i. e. $n(H_2) = 1$ mol

The amount of water is decreased in the solution by:

$n(H_2O) = 2$ mol

$m(H_2O) = 36$ g

Before electrolysis:

$m(\text{solution NaCl}) = V\rho = 200\ cm^3 \times 1.10\ g\ cm^{-3} = 220\ g$

$$\%\ NaCl = \frac{23.4\ g}{220\ g} \times 100 = 10.64$$

After electrolysis:

m(solution NaCl) = 220 g – 36 g = 184 g

$$\%\ \text{NaCl} = \frac{23.4\ \text{g}}{184\ \text{g}} \times 100 = 12.72$$

PROBLEM 3

Equal volumes (10 cm^3) of 0.01-molar solutions of CH_3COOH and HClO were mixed and then diluted to a total volume of 100 cm^3. Ionisation constant of CH_3COOH is equal to 1.8×10^{-5} and that for HClO is $3,7 \times 10^{-8}$.

Problems:

Calculate:

3.1 degree of ionisation for each of the acids in the solution,

3.2 degree of ionisation of HClO if the diluted solution would not contain CH_3COOH,

3.3 pH value for the solution containing at the same time CH_3COOH and HClO.

SOLUTION

CH_3COOH: K_1, α_1, c_1

HClO: K_2, α_2, c_2

$c_1 = c_2 = 1 \times 10^{-3}$ mol dm^{-3} = c

3.1
$$K_1 = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]} = \frac{(\alpha_1 + \alpha_2)c \times \alpha_1 c}{(1-\alpha_1)\,c} = \frac{(\alpha_1 + \alpha_2)\,\alpha_1 c}{1-\alpha_1} \qquad (1)$$

$$K_2 = \frac{[H_3O^+]\,[ClO^-]}{[HClO]} = \frac{(\alpha_1 + \alpha_2)\,\alpha_1 c}{1-\alpha_2} \qquad (2)$$

$K_1 >> K_2$, therefore also $\alpha_1 >> \alpha_2$ and $\alpha_1 + \alpha_2 \approx \alpha_1$

$$K_1\,(1 - \alpha_1) = \alpha_1^2\,c$$

$$c\,\alpha_1^2 + K_1\,\alpha_1 - K_1 = 0$$

$$\alpha_1 = 0,125$$

When (2) is divided by (1):

$$\frac{K_2}{K_1} = \frac{(1-\alpha_1)\,\alpha_2}{(1-\alpha_2)\,\alpha_1}$$

After substitution of α_1: $\alpha_2 = 2.94 \,.\, 10^{-4}$

3.2 $K_2 = \dfrac{\alpha_2^2\ c}{1-\alpha_2}$

$\alpha_2 << 1$

$K_2 = \alpha_2^2\ c$

$\alpha_2 = 6{,}08\ .\ 10^{-3}$

3.3 $[H_3O^+] = \alpha_1 c + \alpha_2 c = (\alpha_1 + \alpha_2)\ c = (0{,}125 + 2{,}94 \times 10^{-4}) \times 10^{-3} \approx 1{,}25 \times 10^{-4}$ mol dm^{-3}

<u>pH = 3,9</u>

PROBLEM 3

The following 0.2 molar solutions are available:

A: HCl	**B**: HSO_4^-	**C**: CH_3COOH	**D**: NaOH
E: CO_3^{2-}	**F**: CH_3COONa	**G**: HPO_4^{2-}	**H**: H_2SO_4

Problems:

1. Determine the concentration of H_3O^+ ions in solution **C**.
2. Determine pH value in solution **A**.
3. Write an equation for the chemical reaction that takes place when substances **B** and **E** are allowed to react and mark conjugate acid-base pairs.
4. Compare acid-base properties of substances **A**, **B**¸ and **C** and determine which one will show the most basic properties. Explain your decision.
5. Write a chemical equation for the reaction between substances **B** and **G**, and explain the shift of equilibrium.
6. Write a chemical equation for the reaction between substances **C** and **E**, and explain the shift of equilibrium.
7. Calculate the volume of **D** solution which is required to neutralise 20.0 cm^3 of **H** solution.
8. What would be the volume of hydrogen chloride being present in one litre of **A** solution if it were in gaseous state at a pressure of 202.65 kPa and a temperature of 37 °C?

Ionisation constants:

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$	$K_a = 1.8 \times 10^{-5}$
$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$	$K_a = 4.4 \times 10^{-7}$
$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$	$K_a = 4.7 \times 10^{-11}$
$HSO_4^{2-} + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$	$K_a = 1.7 \times 10^{-2}$
$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$	$K_a = 4.4 \times 10^{-13}$

Relative atomic masses:

A_r(Na) = 23; A_r(S) = 32; A_r(O) = 16.

SOLUTION

1. $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{[H_3O^+]^2}{c}$$

$$[H_3O^+] = \sqrt{K_a\ c} = \sqrt{1.8\times10^{-5}\times0.2} = 1.9\times10^{-3}\ \text{mol dm}^{-3}$$

2. pH = - log $[H_3O^+]$ = - log 0.2 = 0.7

3. $$\underset{A_1}{HSO_4^{2-}} + \underset{B_2}{CO_3^{2-}} \rightleftharpoons \underset{B_1}{SO_4^{2-}} + \underset{A_2}{HCO_3^-}$$

4. By comparison of the ionisation constants we get:

$K_a(HCl) > K_a(HSO_4^-) > K_a(CH_3COOH)$

Thus, the strength of the acids in relation to water decreases in the above given order.

CH_3COO^- is the strongest conjugate base, whereas Cl^- is the weakest one.

5. $HSO_4^- + HPO_4^{2-} \rightleftharpoons H_2PO_4^- + SO_4^{2-}$

$K_a(HSO_4^-) >> K_a(HPO_4^{2-})$

Equilibrium is shifted to the formation of $H_2PO_4^-$ and SO_4^{2-}.

6. $CH_3COOH + CO_3^{2-} \rightleftharpoons CH_3COO^- + HCO_3^-$

$CH_3COO^- + HCO_3^- \rightleftharpoons CH_3COO^- + H_2CO_3$

$K_a(CH_3COOH) > K_a(H_2CO_3) > K_a(HCO_3^-)$

Equilibrium is shifted to the formation of CH_3COO^- a H_2CO_3.

7. $n(H_2SO_4) = c\ V = 0.2\ \text{mol dm}^{-3} \times 0.02\ \text{dm}^3 = 0.004\ \text{mol}$

$$V(\text{0.2 molar NaOH}) = \frac{n}{c} = \frac{0.008\ \text{mol}}{0.2\ \text{mol dm}^{-3}} = 0.04\ \text{dm}^3$$

8. $$V(\text{HCl}) = \frac{n\,R\,T}{p} = \frac{0.2\text{ mol} \times 8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 310\text{ K}}{202.65\text{ kPa}} = 2.544\text{ dm}^3$$

PROBLEM 2

An alloy prepared for experimental purposes contains aluminium, zinc, silicon, and copper. If 1000 mg of the alloy are dissolved in hydrochloric acid, 843 cm^3 of hydrogen (0 °C, 101.325 kPa) are evolved and 170 mg of an undissolved residue remain. A sample of 500 mg of the alloy when reacted with a NaOH solution produces 517 cm^3 of hydrogen at the above conditions and in this case remains also an undissolved fraction.

Problem:

2.1 Calculate the composition of the alloy in % by mass.

Relative atomic masses:

A_r(Al) = 26.98; A_r(Zn) = 65.37; A_r(Si) = 28.09; A_r(Cu) = 63.55.

SOLUTION

2.1 HCl dissolves: Al, Zn

NaOH dissolves: Al, Zn, Si

$$\frac{0.843\ \text{dm}^3}{22.414\ \text{dm}^3\ \text{mol}^{-1}} = 37.61\ \text{mmol H}_2 \qquad \text{(Al, Zn)}$$

$$\frac{2 \times 0.517\ \text{dm}^3}{22.414\ \text{dm}^3\ \text{mol}^{-1}} = 46.13\ \text{mmol H}_2 \qquad \text{(Al, Zn, Si)}$$

The difference of 8.52 mmol H_2 corresponds to 4.26 mmol Si

<u>Si</u>: $m(\text{Si}) = 4.26\ \text{mmol} \times 28.09\ \text{g mol}^{-1} = 119.7\ \text{mg}$

$$\%\ \text{Si} = \frac{119.7\ \text{mg}}{1000\ \text{mg}} \times 100 = 11.97$$

<u>Cu</u>: $m(\text{Si + Cu}) = 170\ \text{mg}$

$m(\text{Cu}) = 170\ \text{mg} - 119.7\ \text{mg} = 50.3\ \text{mg}$ (in 1000 mg of the alloy)

% Cu = 5.03

Al: m(Zn + Al) = 1000 mg – 170 mg = 830 mg

x mg Al gives $\frac{3}{2}\times\frac{x}{26.98}$ mmol H_2

(830 – x) mg Zn gives $\frac{830-x}{65.37}$ mmol H_2

$$\frac{3}{2}\times\frac{x}{26.98}+\frac{830-x}{65.37}=37.61\text{ mmol }H_2$$

x = 618.2 mg Al (in 1000 mg of the alloy)

% Al = 61.82

Zn: m(Zn) = 830 mg – 618.2 mg = 211.8 mg (in 1000 mg of the alloy)

% Zn = 21.18

PROBLEM 3

A sample of 1500 mg of an alloy that contains silver, copper, and chromium is dissolved and the solution containing Ag^+, Cu^{2+}, and Cr^{3+} ions, is diluted to exactly 500 cm^3. One tenth of the volume of that solution is taken for further procedure:

After elimination of silver and copper, chromium is oxidised in it according to the following unbalanced equation:

$$OH^- + Cr^{3+} + H_2O_2 \rightarrow CrO_4^{2-} + H_2O$$

Then 25.00 cm^3 of a 0.100 molar Fe(II) salt solution are added. The following reaction (written in an unbalanced form) is taking place:

$$H^+ + Fe^{2+} + CrO_4^{2-} \rightarrow Fe^{3+} + Cr^{3+} + H_2O$$

According to the unbalanced equation:

$$H^+ + Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+} + H_2O$$

a volume of 17.20 cm^3 of a 0.020-molar $KMnO_4$ solution is required for an oxidation of the Fe(II) salt which remains unoxidized in the solution.

In another experiment, a volume of 200 cm^3 of the initial solution is electrolysed. Due to secondary reactions, the efficiency of the electrolysis is 90 % for metals under consideration. All three metals are quantitatively deposited in 14.50 minutes by passing a current of 2 A through the solution.

Problem:

3.1 Balance the three chemical equations and calculate the composition of the alloy in % by mass.

Relative atomic masses: $A_r(Cu) = 63.55$; $A_r(Ag) = 107.87$; $A_r(Cr) = 52.00$

SOLUTION

3.1 Equations:

$$10\ OH^- + 2\ Cr^{3+} + 3\ H_2O_2 \rightarrow 2\ CrO_4^{2-} + 8\ H_2O$$

$$8\ H^+ + 3\ Fe^{2+} + CrO_4^{2-} \rightarrow 3\ Fe^{3+} + Cr^{3+} + 4\ H_2O$$

$$8\ H^+ + 5\ Fe^{2+} + MnO_4^- \rightarrow 5\ Fe^{3+} + Mn^{2+} + 4\ H_2O$$

Content of Cr:

$17.20 \times 0.020 = 0.344$ mmol $KMnO_4$

$5 \times 0.344 = 1.72$ mmol Fe^{2+}

Reacted: $25 \times 0.1 - 1.72 = 0.78$ mmol Fe^{2+}

It corresponds:

$$\frac{0.78}{3} = 0.26 \text{ mmol Cr in 150 mg of the alloy}$$

m(Cr) = 2.6 mmol × 52 g mol^{-1} = 135.2 mg in 1500 mg of the alloy

% Cr = 9.013

Content of Cu and Ag:

Q = 40.575 mF / 1500 mg	(1087.4 mAh)
Q_{Cr} = 2.6 × 3 = 7.8 mF	(209 mAh)
$Q_{(Cu+Ag)}$ = 40.575 – 7.8 = 32.775 mF	(878.4 mAh)

(F = Faraday's charge)

m(Cu + Ag) = m(alloy) – m(Cr) = 1500 – 135.2 = 1364.8 mg

For deposition of copper: $\frac{2\,x}{63.55}$ mF

For deposition of silver: $\frac{1364.8 - x}{107.87}$ mF

$$32.775 = \frac{2\,x}{63.55} + \frac{1364.8 - x}{107.87}$$

x = 906.26

m(Cu) = 906.26 mg in 1500 mg of the alloy

m(Ag) = 458.54 mg in 1500 mg of the alloy

% Cu = 60.4 % Ag = 30.6

PROBLEM 4

The pH value of a solution containing 3 % by mass of formic acid (ρ = 1.0049 g cm^{-3}) is equal to 1.97.

Problem:

4.1 How many times should the solution be diluted to attain a tenfold increase in the value of ionisation degree?

Relative atomic masses: A_r(H) = 1.01; A_r(C) = 12.01; A_r(O) = 16.

SOLUTION

4.1 $$c_1 = \frac{n_1}{V} = \frac{\dfrac{1004.9 \text{ g} \times 0.03}{45.03 \text{ g mol}^{-1}}}{1 \text{ dm}^3} = 6.55 \times 10^{-1} \text{ mol dm}^{-3}$$

pH = 1.97; $[H^+] = 1.0715 \times 10^{-2}$ mol dm^{-3}

$$\alpha_1 = \frac{[H^+]}{c_1} = 0.01636 \qquad (1.636 \text{ \%})$$

<u>Calculation of c_2 after dilution</u> (two alternative solutions):

a) α_1 – before dilution; α_2 – after dilution

$$K_a = \frac{\alpha_1 \, c_1}{1 - c_1} \qquad (1)$$

$$K_a = \frac{\alpha_2^2 \, c_2}{1 - \alpha_2} = \frac{(10 \, \alpha_1)^2 \, c_2}{1 - 10 \, \alpha_1} \qquad (2)$$

From equations (1) and (2):

$$\frac{c_1}{c_2} = \frac{100 \, (1 - \alpha_1)}{1 - 10 \, \alpha_1} = 117.6$$

b) $$K_a = \frac{[H^+]^2}{c - [H^+]} = \frac{(1.0715 \times 10^{-4})^2}{0.655 - 1.0715 \times 10^{-2}} = 1.78 \times 10^{-4}$$

$$c_2 = \frac{K_a\ (1 - 10\ \alpha_1)}{(10\ \alpha_1)^2} = 5.56 \times 10^{-3}\ \text{mol dm}^{-3}$$

$$\frac{c_1}{c_2} = \frac{6.55 \times 10^{-1}\ \text{mol dm}^{-3}}{5.56 \times 10^{-3}\ \text{mol dm}^{-3}} = 117.8$$

PROBLEM 7

The density of a sulphuric acid solution in a charged lead accumulator should be equal to ρ = 1.28 g cm^{-3} which corresponds to the solution containing 36.87 % of H_2SO_4 by mass. In a discharged lead accumulator it should not decrease under the value of ρ = 1.10 g cm^{-3} which corresponds to the 14.35 % solution of sulphuric acid.

(Faraday's constant F is equal to 26.8 Ah mol^{-1}.)

Problems:

7.1 Write the equation for a total electrochemical reaction that takes place in the lead accumulator when it is charged and discharged.

7.2 Calculate the masses of H_2O and H_2SO_4 being consumed or formed according to the equation in No 1.

7.3 Calculate the mass of H_2SO_4 that is required to be added to a led accumulator with a capacity of 120 Ah if the content of H_2SO_4 is to be in the range as given in the task.

7.4 Calculate the difference in volumes of the sulphuric acid solutions in a charged and a discharged lead accumulator with a capacity of 120 Ah.

SOLUTION

7.1 $$PbO_2 + Pb + 2\,H_2SO_4 \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftarrows}} 2\,PbSO_4 + 2\,H_2O$$

7.2 $n(H_2SO_4) = 2$ mol $n(H_2O) = 2$ mol

$m(H_2SO_4) = 196$ g $m(H_2O) = 36$ g

Discharging: $\Delta m(H_2SO_4) = -196$ g

$\Delta m(H_2O) = +36$ g

Charging: $\Delta m(H_2SO_4) = +196$ g

$\Delta m(H_2O) = -36$ g

7.3 The mass of H_2SO_4 required:

26.8 Ah corresponds to 98 g H_2SO_4

120 Ah corresponds to 438.8 g H_2SO_4

Analogously:

26.8 Ah corresponds to 18 g H_2O

120 Ah corresponds to 80.6 g H_2O

Discharged lead accumulator:

mass of H_2SO_4 solution – m

mass of H_2SO_4 – m_1

mass fraction of H_2SO_4 – $w_1 = 0.1435$

density of H_2SO_4 solution – $\rho_1 = 1.10\ \text{g cm}^{-3}$

Charged lead accumulator:

mass of H_2SO_4 formed – $m_2 = 438.8\ \text{g}$

mass of H_2O consumed – $m_3 = 80.6\ \text{g}$

mass fraction of H_2SO_4 – $w_2 = 0.3687$

density of the H_2SO_4 solution – $\rho_2 = 1.28\ \text{g cm}^{-3}$

Because:

$$w_1 = \frac{m_1}{m} \qquad \text{(a)}$$

$$w_2 = \frac{m_1 + m_2}{m + m_2 - m_3} \qquad \text{(b)}$$

We get a system of equations (a) and (b) which are solved for m_1 and m:

$$m_1 = 195.45\ \text{g}$$

$$m = 1362\ \text{g}$$

7.4 Volume of the electrolyte V_1 in a discharged lead accumulator:

$$V_1 = \frac{m}{\rho_1} = \frac{1362\ \text{g}}{1.10\ \text{g cm}^{-3}} = 1238.2\ \text{cm}^3$$

Volume of the electrolyte V_2 in a charged lead accumulator:

$$V_2 = \frac{m + m_2 - m_3}{\rho_2} = \frac{1720.2\ \text{g}}{1.28\ \text{g cm}^{-3}} = 1343.9\ \text{cm}^3$$

Difference in the volumes:

$$\Delta V = V_2 - V_1 = 1343.9 - 1238.2 = 105.7\ \text{cm}^3$$

PROBLEM 5

Two copper(I) salts of the organic acids HA and HB, slightly soluble in water, form a saturated solution in buffer of a given pH.

Problems:

5.1 What will be the concentration of Cu^+ cations in the solution if the solubility products of the two salts are K_s(CuA) and K_s(CuB) and the ionisation constants of the acids are K_a(HA) and K_a(HB)?

SOLUTION

5.1 Equations for the total amounts of substances of the particles A, B, and Cu are as follows:

$a = n(A^-) + n(HA) + n(CuA)$

$b = n(B^-) + n(HB) + n(CuB)$

$m = n(Cu^+) + n(CuA) + n(CuB)$

The amounts of precipitates are eliminated from the equations:

$a + b - m = n(A^-) + n(HA) + n(B^-) + n(HB) - n(Cu^+) = 0$

because, when forming a system of both solid salts, the total number of particles A and B (*a* + *b*) must be equal to the total number of cations Cu^+, i. e. to the value of *m*. When the amounts of substances are divided by the volume of the solution, we get concentrations, and thus:

$$[A^-] + [HA] + [B^-] + [HB] = [Cu^+] \qquad (1)$$

$$K_s(CuA) = [Cu^+][A^-] \quad \Rightarrow \quad [A^-] = \frac{K_s(CuA)}{[Cu^+]} \qquad (2)$$

$$K_s(CuB) = [Cu^+][B^-] \quad \Rightarrow \quad [B^-] = \frac{K_s(CuB)}{[Cu^+]} \qquad (3)$$

$$K_a(HA) = \frac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad [HA] = \frac{[H^+][A^-]}{K_a(HA)} \qquad (4)$$

$$K_a(\mathrm{HB}) = \frac{[\mathrm{H}^+][\mathrm{B}^-]}{[\mathrm{HB}]} \quad \Rightarrow \; [\mathrm{HB}] = \frac{[\mathrm{H}^+][\mathrm{B}^-]}{K_a(\mathrm{HB})} \tag{5}$$

By substituting (4) and (5) into (1):

$$[\mathrm{Cu}^+] = [\mathrm{A}^-]\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HA})}\right) + [\mathrm{B}^-]\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HB})}\right) \tag{6}$$

By substituting (2) and (3) into (6):

$$[\mathrm{Cu}^+] = \frac{K_\mathrm{s}(\mathrm{CuA})}{[\mathrm{Cu}^+]}\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HA})}\right) + \frac{K_\mathrm{s}(\mathrm{CuB})}{[\mathrm{Cu}^+]}\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HB})}\right) \tag{7}$$

$$[\mathrm{Cu}^+] = \sqrt{K_\mathrm{s}(\mathrm{CuA})\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HA})}\right) + K_\mathrm{s}(\mathrm{CuB})\left(1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}(\mathrm{HB})}\right)}$$

PROBLEM 6

Amino acids can be determined by measuring the volume of nitrogen released in their reaction with nitrous acid (Van Slyke's method), for example:

$CH_3CH(NH_2)COOH + HNO_2 \rightarrow CH_3CH(OH)COOH + N_2 + H_2O$

Another method consists of the reaction of amino acids with a volumetric solution of perchloric acid, for example:

$CH_3CH(NH_2)COOH + HClO_4 \rightarrow CH_3CH(N^+H_3)COOH + ClO_4^-$

The excess of the perchloric acid is determined then by titration with a volumetric solution of sodium acetate (carried out in a non-aqueous solution).

50.0 cm^3 of a 0.100-normal solution of perchloric acid were added to a sample of glycine in glacial acetic acid. The excess of the perchloric acid was determined after the reaction by titration with 0.150-normal volumetric solution of sodium acetate. The consumption was 16.0 cm^3.

Problem:

6.1 What would be the volume of the nitrogen released at a pressure of 102 658 Pa and a temperature of 20 °C when assumed that the same quantity of sample were analysed by the Van Slyke's method?

SOLUTION

6.1 $n(HClO_4) = V\,c = 0.0500\text{ dm}^3 \times 0.100\text{ mol dm}^{-3} = 0.00500\text{ mol}$

$n(NaAc) = 0.0160\text{ dm}^3 \times 0.150\text{ mol dm}^{-3} = 0.00240\text{ mol}$

Consumed in the reaction:

$n(HClO_4) = (0.00500 - 0.00240)\text{ mol} = 0.00260\text{ mol}$

$V(HClO_4) = 0.0260\text{ dm}^3$

Since:

$n(HClO_4) = n(\text{glycine}) = n(N_2) = 0.0260\text{ mol}$

then:

$$V(N_2) = \frac{nRT}{p} = \frac{0.0260\text{ mol} \times 8.314\text{ Jmol}^{-1}\text{K}^{-1} \times 293.1\text{ K}}{102.658\text{ kPa}} = 0.617\text{ dm}^3$$

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THEORETICAL PROBLEMS

PROBLEM 1

a) A chromium ore which does not contain water, consists of: $Fe(CrO_2)_2$, $Mg(CrO_2)_2$, $MgCO_3$, and $CaSiO_3$.

b) It was found by analysis the ore contains 45.6 % of Cr_2O_3, 7.98 % of Fe_2O_3, and 16.12 % of MgO.

c) When the ore was treated with a concentrated hydrochloric acid, chromium compounds being present in the ore did not react with the acid.

d) When the reaction was finished, the ore was thoroughly washed with water (till the reaction with Cl^- was negative) and the solid residue was dried to a constant mass.

Problems:

1.1 Write stoichiometric and ionic equations for the reactions taking place when the ore is treated with the hydrochloric acid as given in c).

1.2 Calculate:

- the content of the compounds (in mass %) present in the ore,
- amounts of substances of the compounds present in the ore.

1.3 Calculate the content of Cr_2O_3 (in mass %) in the dried residue obtained according to d).

1.4 A glass tube was filled with a sufficient amount of granulated CaO, the total mass of the filled tube having been 412.02 g. A gas formed by the reaction as given in c), was dried and then transmitted through the glass tube. Calculate the mass of the glass tube with its filling after the reaction was finished.

Relative atomic masses: $A_r(Cr) = 52.01$; $A_r(Fe) = 55.85$; $A_r(Mg) = 24.32$; $A_r(Ca) = 40.08$;
$A_r(Si) = 28.09$; $A_r(C) = 12.01$; $A_r(O) = 16.00$.

SOLUTION

1.1 $MgCO_3 + 2\,HCl \rightarrow MgCl_2 + CO_2 + H_2O$

$MgCO_3 + 2\,H^+ \rightarrow Mg^{2+} + CO_2 + H_2O$

$CaSiO_3 + 2\,HCl \rightarrow CaCl_2 + SiO_2 + H_2O$

$CaSiO_3 + 2\,H^+ \rightarrow Ca^{2+} + SiO_2 + H_2O$

1.2 The total amount of iron is in the form of $Fe(CrO_2)_2$:

Since:

$$Fe_2O_3 \triangleq 2\ Fe(CrO_2)_2$$

$M_r(Fe_2O_3) = 159.70$

$M_r(Fe(CrO_2)_2) = 223.87$ % $Fe_2O_3 = 7.98$

$$\textbf{\% Fe(CrO}_\mathbf{2}\textbf{)}_\mathbf{2} = \frac{2 \times 223.87}{159.70} \times 7.98 = \mathbf{22.37}$$

The difference between the total amount of Cr_2O_3 and that being contained in $Fe(CrO_2)_2$ corresponds to the amount of Cr_2O_3, having been in the form of $Mg(CrO_2)_2$.

% Cr_2O_3 in $Fe(CrO_2)_2$:

$$\begin{array}{lcc} & Fe(CrO_2)_2 \triangleq & Cr_2O_3 \\ M_r: & 223.87 & 152.02 \end{array}$$

$$\textbf{\% Cr}_\mathbf{2}\textbf{O}_\mathbf{3} = \frac{152.02}{223.87} \times 22.37 = \mathbf{15.19}$$

% Cr_2O_3 in $Mg(CrO_2)_2$: $45.5 - 15.19 = 30.41$

Content of $Mg(CrO_2)_2$:

$$\begin{array}{lcc} & Cr_2O_3 \triangleq & Mg(CrO_2)_2 \\ M_r: & 152.02 & 192.34 \end{array}$$

$$\textbf{\% Mg(CrO}_\mathbf{2}\textbf{)}_\mathbf{2} = \frac{192.34}{152.02} \times 30.41 = \mathbf{38.47}$$

The difference between the total amount of MgO in the ore and that corresponding to $Mg(CrO_2)_2$, is contained in $MgCO_3$. % MgO and % $MgCO_3$ can be calculated analogously as it is given above.

$$\begin{array}{lcc} & Mg(CrO_2)_2 \triangleq & MgO \\ M_r: & 192.34 & 40.32 \end{array}$$

$$\textbf{\% MgO} = \frac{40.32}{192.34} \times 38.47 = \mathbf{8.06}$$

$$MgO \triangleq MgCO_3$$

$$\begin{array}{lcc} M_r: & 40.32 & 84.32 \end{array}$$

$$\textbf{\% MgCO}_\mathbf{3} = \frac{84.32}{40.32} \times 8.06 = \mathbf{16.86}$$

Content of $CaSiO_3$ is obtained as complementary value to 100 %.

% $CaSiO_3$ = 100 – (22.37 + 38.47 + 16.86) = **22.30**

One kilogram of the ore contains:

223.7 g of $Fe(CrO_2)_2 \triangleq$ 1 mol

384.7 g of $Mg(CrO_2)_2 \triangleq$ 2 mol

168.6 g of $MgCO_3 \triangleq$ 2 mol

223.0 g of $CaSiO_3 \triangleq$ 2 mol

1.3 In order to simplify the problem we can assume that the hydrochloric acid reacts with 1 kg of the ore, i. e. with 168.6 g of $MgCO_3$ and with that CaO which is contained in 223.0 g $CaSiO_3$, i. e. with 107.65 of CaO.

Thus, 276.25 g of the ore (168.6 g + 107.65 g) reacted while 723.75 g remain unreacted.

One kilogram of the ore contains 456 g of Cr_2O_3 (45.6 %) and the same amount remains in the unreacted part that represents:

$$\textbf{\% Cr}_\mathbf{2}\textbf{O}_\mathbf{3} = \frac{456}{723.75} \times 100 = \mathbf{63.0}$$

1.4 The mass of the filling in the tube is increased by the mass of CO_2 formed by decomposition of $MgCO_3$ with hydrochloric acid. From 168.6 g of $MgCO_3$ 87.98 g of CO_2 are formed and thus, the mass of the tube after reaction is 500 g.

PROBLEM 2

A sample of water under investigation had 10° of temporary hardness and 10° of permanent hardness. Hardness of the water was caused by cations Fe^{2+} and Ca^{2+} only.

A volume of 10.00 dm^3 of the water was at disposal. From this volume 100.00 cm^3 were taken for further procedure. The water was oxidised with a H_2O_2 solution and then precipitated with an aqueous ammonia solution. A brown precipitate was dried and after an appropriate heating 0.01432 g of an anhydrous product was obtained.

Problems:

2.1 Calculate the molar ratio of Fe^{2+} : Ca^{2+} in the water under investigation.

2.2 In another experiment, 10.00 dm^3 of the water was used again. The temporary hardness caused by cations Ca^{2+} was removed first and the permanent hardness caused by cations Fe^{2+} was removed by addition of Na_3PO_4. Calculate the mass of the precipitate (in its anhydrous form) on the assumption that only one half of cations Fe^{2+} was oxidised to Fe^{3+} in 10.00 dm^3 of the water analysed. Calculation should be made with an accuracy of one hundredth. Give the molar ratio in integers.

1° of hardness = 10 mg CaO in 1 dm^3 of water.

Relative atomic masses:

A_r(Ca) = 40.08; A_r(Fe) = 55.85; A_r(C) = 12.01;

A_r(H) = 1.01; A_r(P) = 31.00; A_r(O) = 16.00.

SOLUTION

2.1 Anhydrous product: Fe_2O_3

$m(Fe_2O_3)$ = 0.01432 g from 100 cm^3 of water, i. e. 1.432 g from 10 dm^3

1 mol Fe_2O_3 $\Leftrightarrow$ 2 mol FeO

$$n(Fe_2O_3) = \frac{1.432\ \text{g}}{159.7\ \text{g mol}^{-1}} \approx 0.009\ \text{mol}$$

$m(\text{FeO}) = n\,M = 2 \times 0.009\ \text{mol} \times 71.85\ \text{g mol}^{-1} \approx 1.293\ \text{g}$

1° of hardness = 10 mg CaO / dm^3 of water

$$1° \text{ of hardness} = \frac{M(\text{FeO})}{M(\text{CaO})} \times 10 \text{ mg} = 12.81 \text{ mg FeO} / \text{dm3 of water}$$

$$\frac{1.293 \text{ g FeO}}{0.1281 \text{ g FeO}} \approx 10° \text{ of hardness}$$

Since the water has totally 20° of hardness, and 10 ° of hardness fall on FeO, the other 10° of hardness are attributed to CaO which corresponds to 1 g of CaO in 10 dm^3 of the water.

Molar ratio:

$$n(\text{FeO}) : n(\text{CaO}) = \frac{m(\text{FeO})}{M(\text{FeO})} : \frac{m(\text{CaO})}{M(\text{CaO})} = \frac{1.289 \text{ g}}{71.85 \text{ g mol}^{-1}} : \frac{1 \text{ g}}{56.08 \text{ g mol}^{-1}} = 1 : 1$$

2.2 A volume of 10.00 dm^3 of the water contains so much iron that corresponds to 1.293 g of FeO. 50 % of iron (0.6445 g of FeO) were oxidised to Fe(III), and therefore $Fe_3(PO_4)_2$ as well as $FePO_4$ are formed at the same time.

3 mol FeO . . . . . . 1 mol $Fe_3(PO_4)_2$

215.55 g . . . . . . 357.55 g

0.6445 g . . . . . . $\underline{1.0699 \text{ g } Fe_3(PO_4)_2}$

1 mol FeO . . . . . . 1 mol $FePO_4$

71.85 g . . . . . . 150.85 g

0.6445 g . . . . . . $\underline{1.3542 \text{ g } FePO_4}$

Mass of the precipitate: 1.0699 g + 1.3542 g = $\underline{2.4241 \text{ g}}$

PROBLEM 2

An alloy comprises the following metals: cadmium, tin, bismuth, and lead. A sample of this alloy weighing 1.2860 g, was treated with a solution of concentrated nitric acid. The individual compound of metal **A** obtained as a precipitate, was separated, thoroughly washed, dried and calcinated. The mass of the precipitate after the calcination to constant mass, was 0.3265 g.

An aqueous ammonia solution was added in excess to the solution obtained after separation of the precipitate. A compound of metal **B** remained in the solution while all the other metals precipitated in the form of sparingly soluble compounds. The solution was first quantitatively separated from the precipitate, and then hydrogen sulphide was passed through the separated solution to saturation. The resulting precipitate containing metal **B** was separated, washed and dried. The mass of the precipitate was 0.6613 g.

The precipitate containing the compounds of metals **C** and **D** was treated with an excess of a NaOH solution. The solution and the precipitate were then quantitatively separated. A solution of HNO_3 was added to the alkaline solution to reach pH 5 – 6, and an excess of K_2CrO_4 solution was added to the resulting transparent solution. The yellow precipitate was separated, washed and quantitatively transferred to a beaker. Finally a dilute H_2SO_4 solution and crystalline KI were added. Iodine produced as a result of the reaction was titrated with sodium thiosulphate solution in the presence of starch as an indicator. 18.46 cm^3 of 0.1512 normal $Na_2S_2O_3$ solution were required.

The last metal contained in the precipitate as a sparingly soluble compound was transformed to an even less soluble phosphate and its mass was found to be 0.4675 g.

2.1 Write all equations of the chemical reactions on which the quantitative analysis of the alloy sample is based. Name metals **A**, **B**, **C**, and **D**. Calculate the mass percentage of the metals in the alloy.

SOLUTION

2.1 The action of nitric acid on the alloy:

$Sn + 4 HNO_3 \rightarrow H_2SnO_3 + 4 NO_2 + H_2O$

$Pb + 4 HNO_3 \rightarrow Pb(NO_3)_2 + 2 NO_2 + 2 H_2O$

$Bi + 6 HNO_3 \rightarrow Bi(NO_3)_3 + 3 NO_2 + 3 H_2O$

$Cd + 4\ HNO_3 \rightarrow Cd(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

Weight form of tin determination:

$H_2SnO_3 \rightarrow SnO_2 + H_2O$

Calculation of tin content in the alloy:

$M(Sn) = 118.7\ g\ mol^{-1}$; $M(SnO_2) = 150.7\ g\ mol^{-1}$

$$\frac{m(\text{Sn})}{m(\text{SnO}_2)} = \frac{M(\text{Sn})}{M(\text{SnO}_2)}; \qquad m(\text{Sn}) = \frac{118.7\ \text{g mol}^{-1} \times 0.3265\ \text{g}}{150.7\ \text{g mol}^{-1}} = 0.2571\ \text{g}$$

Mass percentage of tin (metal A) in the alloy:

$$w(\text{Sn}) = \frac{0.2571\ \text{g}}{1.2860\ \text{g}} = 0.1999 = 19.99\ \%$$

The reactions taking place in the excess of aqueous ammonia solution:

$Pb(NO_3)_2 + 2\ NH_4OH \rightarrow Pb(OH)_2\downarrow + 2\ NH_4NO_3$

$Bi(NO_3)_3 + 3\ NH_4OH \rightarrow Bi(OH)_3\downarrow + 3\ NH_4NO_3$

$Cd(NO_3)_2 + 4\ NH_4OH \rightarrow \underset{\text{solution}}{[Cd(NH_3)_4](NO_3)_2} + 4\ H_2O$

Saturating of the solution with hydrogen sulphide:

$[Cd(NH_3)_4](NO_3)_2 + 2\ H_2S \rightarrow CdS\downarrow + 2\ NH_4NO_3 + (NH_4)_2S$

Calculation of the cadmium content in the alloy:

$M(Cd) = 112.4\ g\ mol^{-1}$; $M(CdS) = 144.5\ g\ mol^{-1}$

$$m(\text{Cd}) = \frac{112.4\ \text{g mol}^{-1} \times 0.6613\ \text{g}}{144.5\ \text{g mol}^{-1}} = 0.5143\ \text{g}$$

Mass percentage of cadmium (metal B) in the alloy:

$$w(\text{Cd}) = \frac{0.5143\ \text{g}}{1.2860\ \text{g}} = 0.3999 = 39.99\ \%$$

The reactions taking place in the excess of sodium hydroxide solution:

The action of excess sodium hydroxide on lead(II) and bismuth(III) hydroxides:

$Pb(OH)_2 + 2\ NaOH \rightarrow \underset{\text{solution}}{Na_2[Pb(OH)_4]}$

$Bi(OH)_3 + NaOH \rightarrow$ no reaction

Acidification of the solution with nitric acid (pH = 5 – 6):

$Na_2[Pb(OH)_4] + 4\ HNO_3 \rightarrow Pb(NO_3)_2 + 2\ NaNO_3 + 4\ H_2O$

The reaction with K_2CrO_4:

$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4\downarrow + 2\ KNO_3$

The reactions on which the quantitative determination of lead in $PbCrO_4$ precipitate is based:

$2\ PbCrO_4 + 6\ KI + 8\ H_2SO_4 \rightarrow 3\ I_2 + 2\ PbSO_4 + 3\ K_2SO_4 + Cr_2(SO_4)_3 + 8\ H_2O$

$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$

Percentage of lead (metal C) in the alloy:

$$w(\text{Pb}) = \frac{c(\text{Na}_2\text{S}_2\text{O}_3) \times V(\text{Na}_2\text{S}_2\text{O}_3) \times M(\text{Pb})}{m(\text{alloy}) \times 3}$$

(One Pb^{2+} ion corresponds to one CrO_4^{2-} ion which accepts 3 electrons in the redox reaction considered.)

$$w(\text{Pb}) = \frac{0.1512\ \text{mol dm}^{-3} \times\ 0.01846\ \text{dm}^3 \times\ 207.2\ \text{g mol}^{-1}}{1.286\ \text{g} \times 3} = 0.1499 = 14.99\ \%$$

In order to convert bismuth(III) hydroxide to phosphate it is necessary:

a) to dissolve the bismuth(III) hydroxide in an acid:

$Bi(OH)_3 + 3\ HNO_3 \rightarrow Bi(NO_3)_3 + 3\ H_2O$

b) to precipitate Bi^{3+} ions with phosphate ions:

$Bi(NO_3)_3 + K_3PO_4 \rightarrow BiPO_4\downarrow + 3\ KNO_3$

Calculation of the bismuth content in the alloy:

$M(\text{Bi}) = 209\ \text{g mol}^{-1}$; $M(\text{BiPO}_4) = 304\ \text{g mol}^{-1}$

$$m(\text{Bi}) = \frac{209\ \text{g mol}^{-1} \times 0.4676\ \text{g}}{304\ \text{g mol}^{-1}} = 0.3215\ \text{g}$$

Percentage of bismuth (metal D) in the alloy:

$$w(\text{Bi}) = \frac{0.3215\ \text{g}}{1.2860\ \text{g}} = 0.2500 = 25.00\ \%$$

Composition of the alloy: % Cd = 40, % Sn = 20, % Pb = 15, % Bi = 25

PROBLEM 3

(Chemistry of ions, stoichiometry, redox reactions)

A white crystalline solid compound **A** exhibits the following reactions:

1) The flame of a Bunsen burner is intensively yellow coloured.
2) An aqueous solution of **A** is neutral. Dropwise addition of sulphurous acid (an SO_2 solution) leads to a deep brown solution that is discoloured in the presence of excess of sulphurous acid.
3) If an $AgNO_3$ solution is added to the discoloured solution obtained by 2) and acidified with HNO_3, a yellow precipitate is obtained that is insoluble on addition of NH_3, but can be readily dissolved by adding CN^- or $S_2O_3^{2-}$.
4) If an aqueous solution of **A** is treated with KI and dilute H_2SO_4 a deep brown solution is formed that can be discoloured by addition of sulphurous acid or a $Na_2S_2O_3$ solution.
5) An amount of 0.1000 g of **A** is dissolved in water, then 0.5 g KI and a few cm^3 of dilute H_2SO_4 are added. The deep brown solution formed is titrated with 0.1000 M $Na_2S_2O_3$ solution until the solution is completely discoloured. The consumption is 37.40 cm^3.

Problems:

3.1 What elements are contained in the compound **A**?

3.2 What compounds can be considered as present on the basis of reactions 1) to 4)? Calculate their molar masses.

3.3 Formulate the reactions corresponding to 2) to 4) for the compounds considered and write the corresponding equations in the ionic form.

3.4 Decide on the basis of 5) which compound is present.

SOLUTION

3.1 The solid must contain Na and I. The yellow colouration of the flame of the Bunsen burner indicates the presence of Na. A yellow silver salt that is dissolved only by strong complexing agents such as CN^- or $S_2O_3^{2-}$, must be AgI.

3.2 Reactions 1) to 4) indicate an Na salt of an oxygen containing acid of iodine:

Both SO_2 and I^- are oxidised. While in the first case I^- is formed with an intermediate of I_2 (or I_3^-, brown solution), in the second I_2 (or I_3^-) is formed.

As the solution of **A** is neutral, $NaIO_3$ and $NaIO_4$ come into consideration.

$M(NaIO_3) = 22.99 + 126.905 + 3 \times 16.000 = 197.895 = 197.90\ g\ mol^{-1}$

$M(NaIO_4) = 22.99 + 126.905 + 4 \times 16.000 = 213.895 = 213.90\ g\ mol^{-1}$

3.3 $2\ IO_3^- + 4\ H_2O + 5\ SO_2 = 5\ HSO_4^- + 3\ H^+ + I_2$

$I_2 + SO_2 + 2\ H_2O = HSO_4^- + 3\ H^+ + 2\ I^-$

$IO_4^- + 7\ I^- + 8\ H^+ = 4\ I_2 + 4\ H_2O$

$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$

$I_2 + 2\ S_2O_3^{2-} = 2\ I^- + S_4O_6^{2-}$

3.4 Experiment: 0.1000 g of the compound **A** ...... 3.740×10^{-3} moles $S_2O_3^{2-}$

1st hypothesis: The compound is $NaIO_3$.

1 mole $NaIO_3$ . . . . 197.90 g $NaIO_3$ . . . . 6 moles $S_2O_3^{2-}$

0.1000 g $NaIO_3$ . . . . $\dfrac{0.1000 \times 6}{197.90} = 3.032 \times 10^{-3}$ moles $S_2O_3^{2-}$

The hypothesis is false.

2nd hypothesis: The compound is $NaIO_4$.

mole $NaIO_4$ . . . . 213.90 g $NaIO_4$ . . . . 8 moles $S_2O_3^{2-}$

0.1000 g $NaIO_4$ . . . . $\dfrac{0.1000 \times 8}{213.90} = 3.740 \times 10^{-3}$ moles $S_2O_3^{2-}$

The compound **A** is $NaIO_4$.

PROBLEM 2

Maleic acid (H_2A) is a weak dibasic acid. The correlation between the relative quantities of H_2A, HA^-, A^{2-}:

$$\alpha_0 = \frac{c(H_2A)}{c} \qquad \alpha_1 = \frac{c(HA^-)}{c} \qquad \alpha_2 = \frac{c(A^{2-})}{c}$$

and pH values of the solution show that:

a) $\alpha_0 = \alpha_1$ for pH = 1.92

b) $\alpha_1 = \alpha_2$ for pH = 6.22

Find:

2.1 The values of the dissociation constants of maleic acid for the first (K_1) and the second (K_2) degree of dissociation.

2.2 The values of α_0, α_1, and α_2 for pH = 1.92 and pH = 6.22.

2.3 What is the value of pH when α_1 attains a maximum value? Find the maximum value of α.

2.4 Which of the acid-base indicators in the table are suitable for titration of a 0.1 M solution of maleic acid (as a monobasic and as a dibasic acid) with 0.1 M NaOH?

Fill in the table 1 with the correct answers.

All the activity coefficients should be considered equal to 1.

Indicator	pH interval
Methyl green	0.1 – 2.0
Tropeolin 00	1.4 – 3.2
β-Dinitrophenol	2.4 – 4.0
Bromphenol blue	3.0 – 4.6
Congo red	3.0 – 5.2
Methyl red	4.4 – 6.2
Bromphenol red	5.0 – 6.8
Bromthymol blue	6.0 – 7.6
Phenol red	6.8 – 8.0
Cresol red	7.2 – 8.8

Thymol blue	8.0 – 9.6
Phenolphthalein	8.2 – 10.0
Alizarine yellow	10.1 – 12.1
Tropeolin 0	11.0 – 13.0
1,3,5-Trinitrobenzene	12.2 – 14.0

Table 1

2.1		K_1 =
		K_2 =
2.2	pH = 1.92	α_0 =
		α_1 =
		α_2 =
	pH = 6.22	α_0 =
		α_1 =
		α_2 =
2.3		pH =
		α_1 =
2.4		pH =
	First indicator equivalence point	1. 2. 3. 4.
		pH =
	Second indicator equivalence point	1. 2. 3. 4.

SOLUTION

2.1 $\alpha_0 = \alpha_1$

$K_1 = c_{H^+} = 10^{-pH} = 10^{-1.92} = 1.20 \times 10^{-2}$

$\alpha_1 = \alpha_2$

$K_2 = c_{H^+} = 10^{-pH} = 10^{-6.22} = 6.02 \times 10^{-7}$

2.2 $F = c^2_{H^+} + K_1\, c_{H^+} + K_1\, K_2$

pH = 1.92; $c_{H^+} = 10^{-1.92} = 1.20 \times 10^{-2}$; $F = 2.88 \times 10^{-4}$

$$\alpha_0 = \alpha_1 = \frac{c^2_{H^+}}{F} = \frac{(1.20\,.10^{-2})^2}{2.88\,.10^{-4}} = 0.500$$

$$\alpha_2 = \frac{K_1\, K_2}{F} = \frac{1.20\,.10^{-2} \times 6.02\;.\;10^{-7}}{2.88\,.10^{-4}} = 2.51 \times 10^{-5}$$

pH = 6.22; $c_{H^+} = 10^{-6.22} = 6.02 \times 10^{-7}$; $F = 1.445 \times 10^{-8}$

$$\alpha_0 = \frac{c^2_{H^+}}{F} = \frac{(6.02 \times 10^{-7})^2}{1.445 \times 10^{-8}} = 2.51 \times 10^{-5}$$

$$\alpha_1 = \alpha_2 = \frac{K_1\, K_2}{F} = \frac{1.20 \times 10^{-2} \times 6.02 \times 10^{-7}}{1.445 \times 10^{-8}} = 0.500$$

2.3

$$(\alpha)'_{c_{H^+}} = \frac{\left[K_1 F - K_1\, c_{H^+}\,(2c_{H^+} + K_1\right]}{F^2} = 0$$

$$c^2_{H^+} = K_1 K_2$$

$$c_{H^+} = \sqrt{(1.20 \times 10^{-2} \times 6.02 \times 10^{-7}} = 8.50 \times 10^{-5} \text{ mol dm}^{-3}$$

$F = 1.034 \times 10^{-6}$ pH = 4.07

$$\alpha_1 = \frac{K_1\, c_{H^+}}{F} = \frac{1.20 \times 10^{-2} \times 8.50 \times 10^{-5}}{1.034 \times 10^{-6}} = 0.986$$

The pH and the maximum value of α_1 can be estimated either by calculating α_1 for a set of values of c_{H^+} in the interval $1 \times 10^{-5} – 1 \times 10^{-3}$ mol dm^{-3} or from the condition that α_1 can reach a maximum value only when $\alpha_0 = \alpha_2$

2.4 The first equivalence point is found in the region of the α_1 maximum at pH = 4.07 where $c_{HA^-} = c_{NaHA} = \frac{0.1}{2} = 0.05 \text{ mol dm}^{-3}$.

The second equivalence point is found in the alkaline region, where:

$$c_{OH^-} = c_{HA^-} \qquad c_{A^{2-}} = \frac{0.1}{3} - c_{OH^-} = 0.0333$$

$$c_{H+}^2 = \frac{K_2\, c_{HA^-}}{c_{A^{2-}}} = \frac{K_2\, c_{OH^-}}{c_{A^{2-}}} = \frac{K_2\, K_w}{c_{H^+}\, c_{A^{2-}}}$$

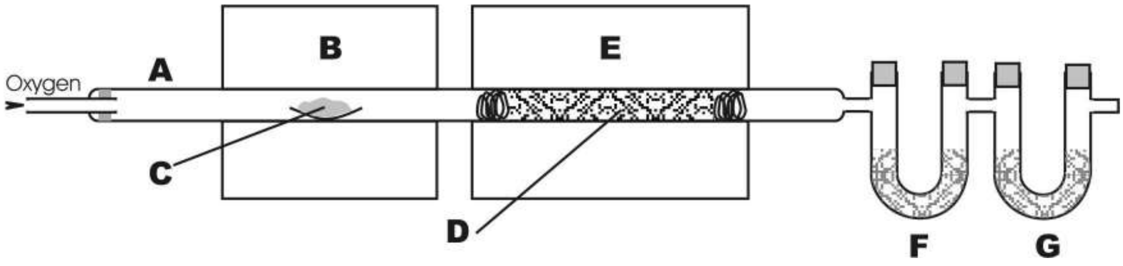
$$c_{H^+} = \sqrt{\frac{K_2\, K_w}{c_{A^{2-}}}} = \sqrt{\frac{6.02\times10^{-7} \times 1\times10^{-14}}{0.0333}} = 4.25\times10^{-10}\ \text{mol dm}^{-3}$$

pH = 9.37

Indicators:

Bromphenol blue, Congo red, thymol blue, phenolphthalein.

PROBLEM 2



Quantitative analysis for carbon and hydrogen was originally carried out using a technique and apparatus (see figure) originally developed in 1831 by the famous chemist Justus Liebig. A carefully weighed sample of organic compound (C) is placed in a combustion tube (A) and vaporized by heating in a furnace (B). The vapours are swept by a stream of oxygen through a heated copper oxide packing (D) and through another furnace (E), which ensures the quantitative oxidation of carbon and hydrogen to carbon dioxide and water. The water vapour is absorbed in a weighed tube (F) containing magnesium perchlorate and the carbon dioxide in another weighed tube (G) containing asbestos impregnated with sodium hydroxide.

A pure liquid sample containing only carbon, hydrogen and oxygen is placed in a 0.57148 g platinum boat, which on reweighing weights 0.61227 g. The sample is ignited and the previously weighed absorption tubes are reweighed. The mass of the water absorption tube has increased from 6.47002 g to 6.50359 g, and the mass of the carbon dioxide tube has increased from 5.46311 g to 5.54466 g.

2.1 Calculate the mass composition of the compound.

2.2 Give the empirical formula of the compound.

To estimate the molar mass of the compound, 1.0045 g was gasified. The volume, measured at a temperature of 350 K and a pressure of 35.0 kPa, was 0.95 dm^3.

2.3 Give the molar mass and the molecular formula of the compound.

2.4 Draw possible structures corresponding to the molecular formula excluding cyclic structures, stereo isomers, peroxides and unsaturated compounds. There are about 15 possibilities. Give 10 of them.

When the compound is heated with a sodium hydroxide solution, two products are formed. Fractional distillation of the reaction mixture yields one of the substances. The other substance is purified by distillation after acidification and appears to be an acid.

2.5 What structures are possible for compound C?

0.1005 g of the acid are dissolved in water and titrated with a sodium hydroxide solution with a concentration of 0.1000 mol dm^{-3}. The indicator changes colour on addition of 16.75 cm^3 of hydroxide solution.

2.6 What was the original substance C?

SOLUTION

2.1 Mass percentage composition: 54.56 % C; 9.21 % H; 36.23 % O

2.2 Empirical formula: C_2H_4O

2.3 Molar mass: 88 g mol^{-1}

Molecular formula: $C_4H_8O_2$

2.4 Possible structures:

1. CH_3-CH_2-CH_2-COOH
2. CH_3-CH(CH_3)-COOH
3. CH_3-O-CO-CH_2-CH_3
4. CH_3-CH_2-O-CO-CH_3
5. CH_3-CH_2-CH_2-O-CO-H
6. CH_3-CH(CH_3)-O-CO-H
7. CH_3-CH_2-CH(OH)-CHO
8. CH_3-CH(OH)-CH_2-CHO
9. CH_2(OH)-CH_2-CH_2-CHO
10. CH_3-C(OH)(CH_3)-CHO
11. CH_2(OH)-CH(CH_3)-CHO
12. CH_3-O-CH_2-CH_2-CHO
13. CH_3-CH_2-O-CH_2-CHO
14. CH_3-O-CH(CH_3)-CHO
15. CH_3-CH_2-CO-CH_2-OH
16. CH_3-CH(OH)-CO-CH_3
17. CH_2(OH)-CH_2-CO-CH_3
18. CH_3-O-CH_2-CO-CH_3

2.5 The possible structures are 3, 4, 5, 6.

2.6 The structure of the compound C is CH_3-CH_2-O-CO-CH_3.

PROBLEM 3

In a chemical factory in which formaldehyde is produced by oxidation of methanol, aqueous solutions containing methanol and formaldehyde are to be analyzed. In order to test the method, experiments are first carried out with known amounts of both methanol and formaldehyde. The following aqueous solutions are used:

Methanol, 5.00 g dm^{-3}
Formaldehyde, 5.00 g dm^{-3}
Potassium dichromate, 3.000×10^{-2} mol dm^{-3}
Ammonium iron(II) sulphate, 0.2000 mol dm^{-3}
Iodine, 0.1000 mol dm^{-3}
Sodium thiosulphate, 0.2000 mol dm^{-3}.

I. 10.00 cm^3 methanol solution and 100.00 cm^3 potassium dichromate solution are mixed, approximately 100 cm^3 concentrated sulphuric acid is added and the solution is allowed to stand for about 30 minutes. Excess dichromate ions are then titrated with iron(II) ions with diphenylamine sulphonic acid as a redox indicator (colour change from red-violet to pale green). The volume of the iron(II) solution consumed is 43.5 cm^3.

II. 10.00 cm^3 of formaldehyde solution and 50.00 cm^3 of iodine solution are mixed. Sodium hydroxide solution is added to alkaline reaction and the mixture is left standing for about 10 minutes. Hydrochloric acid is then added to a neutral reaction, and the excess iodine is determined by titration with thiosulphate, with starch as an indicator. The volume of the thiosulphate solution required is 33.3 cm^{-3}.

3.1 Using the analysis data in I and II calculate the reacting amounts and the molar ratios of methanol/dichromate ions and formaldehyde/iodine.

3.2 Write balanced equations for all reactions described in experiments I and II.

III. It is checked that iodine does not react with methanol. From a solution containing both methanol and formaldehyde, two 10.00 cm^3 samples are taken.

One sample is mixed with 100.00 cm^3 of potassium dichromate solution and concentrated sulphuric acid as in I. Excess dichromate ions consume 4.8 cm^3 of iron(II) solution.

The other sample is mixed with 50.00 cm^3 of iodine solution and treated as in II. Excess iodine consumes 16.50 cm^3 of thiosulphate solution.

3.3 Give balanced equations for the reactions and calculate the contents of methanol and formaldehyde in the solution. Give your answer in g dm^{-3}.

SOLUTION

3.1 Amounts of substance:

methanol	1.56 mol
dichromate ions	3.00 mol
iron(II) ions	8.70 mol

Molar ratio methanol/dichromate: 1 mol $CH_3OH \Rightarrow$ 1 mol $Cr_2O_7^{2-}$

Amounts of substance:

formaldehyde	1.67 mol
iodine	5.00 mol
thiosulphate ions	6.66 mol

Molar ratio formaldehyde/iodine: 1 mol HCHO $\Rightarrow$ 1 mol I_2

3.2 Chemical equations:

$CH_3OH + Cr_2O_7^{2-} + 8\ H^+ \rightarrow CO_2 + 2\ Cr^{3+} + 6\ H_2O$

$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H^+ \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$

$I_2 + 2\ OH^- \rightarrow IO^- + I^- + H_2O$

$HCHO + IO^- + OH^- \rightarrow HCOO^- + I^- + H_2O$

$IO^- + I^- + 2\ H^+ \rightarrow I_2 + H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

In (3), (5), and (6), I_3^- may participate instead of I_2.

As an alternative to (4)

$HCHO + I_2 + 2\ OH^- \rightarrow HCOO^- + 2\ I^- + H_2O$ is acceptable.

3.3 Chemical equations

To the chemical equations above is added

$3\ HCHO + 2\ Cr_2O_7^{2-} + 16\ H^+ \rightarrow 3\ CO_2 + 4\ Cr^{3+} + 11\ H_2O$

Content of methanol: 1.9 g dm^{-3}

Content of formaldehyde: 10.1 g dm^{-3}

PROBLEM 5

Iodine is soluble to a certain extent in pure water. It is, however, more soluble in solutions containing iodide ions. By studying the total solubility of iodine as a function of iodide concentration, the equilibrium constants of the following reactions can be determined:

Equation	Equilibrium constants	
$I_2(s) \rightleftharpoons I_2(aq)$	k_1	(1)
$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$	k_2	(2)
$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$	k_3	(3)

5.1 Give the equilibrium equations for (1) – (3).

Solutions of known potassium iodide concentration $[I^-]_{tot}$ were equilibrated with solid iodine. Subsequent titration with sodium thiosulphate solution served to determine the total solubility of iodine $[I_2]_{tot}$.

The experiments yielded the following results:

$[I^-]_{tot}$ / mmol dm^{-3}	10.00	20.00	30.00	40.00	50.00
$[I^-]_{tot}$ / mmol dm^{-3}	5.85	10.53	15.11	19.96	24.82

5.2 Plot $[I_2]_{tot}$ versus $[I^-]_{tot}$ in a diagram.

5.3 Derive a suitable algebraic expression relating $[I_2]_{tot}$ and $[I^-]_{tot}$.

5.4 Use the graph to determine values of the equilibrium constants k_1, k_2, and k_3.

SOLUTION

5.1 Equilibrium equations

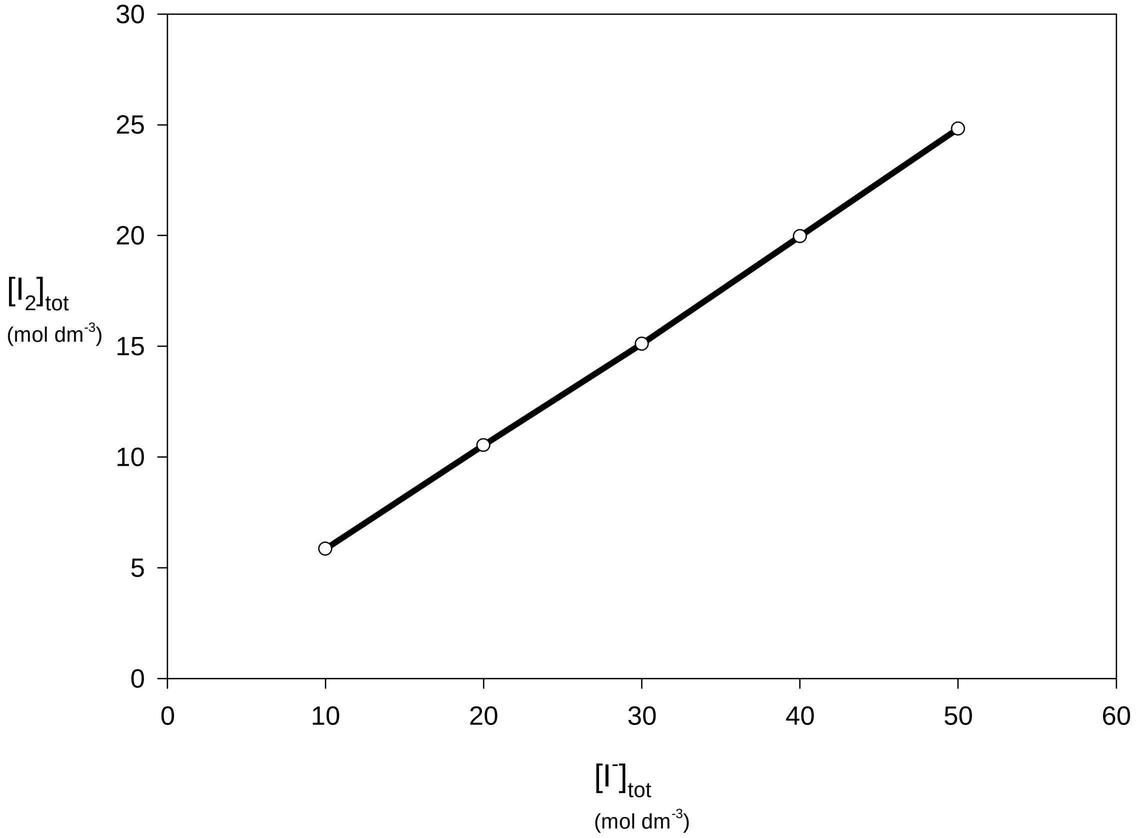
The following relations are valid for the concentrations of the aqueous solutions:

$$[I_2] = k_1$$

$$\frac{[I_3^-]}{[I^-]} = k_2$$

$$\frac{[I_3^-]}{[I_2][I^-]} = k_3 = \frac{k_2}{k_1}$$

5.2 See diagram on the next page.



5.3 The relation between $[I_2]_{tot}$ and $[I^-]_{tot}$ is as follows:

$$[I_2]_{tot} = k_1 + \frac{k_2}{1+k_2}[I^-]_{tot}$$

5.4 $k_1 = 1.04 \times 10^{-3}$ mol dm^{-3} $k_2 = 0.90$ $k_3 = 8.6 \times 10^2$ mol^{-1} dm^3

(These values are calculated by the least square method.)

PROBLEM 7

Calcium oxalate, $CaC_2O_4.H_2O$, is a sparingly soluble salt of analytical and physiological importance. The solubility product is 2.1×10^{-9} at 25 °C. Oxalate ions can protolyse to form hydrogen oxalate ions and oxalic acid. The pK_a values at 25 °C are 1.23 ($H_2C_2O_4$) and 4.28 ($HC_2O_4^-$). At 25 °C the ionic product of water is 1.0×10^{-14}.

7.1 State those expressions for the equilibrium conditions which are of interest for the calculation of the solubility of calcium oxalate monohydrate.

7.2 State the concentration conditions which are necessary for the calculation of the solubility *s* (in mol dm^{-3}) of calcium oxalate in a strong acid of concentration *C*.

7.3 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in a plant cell in which the buffer system regulates the pH to 6.5.

7.4 Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in hydrochloric acid with a concentration of 0.010 mol dm^{-3}. Give the concentration of hydrogen ions in the solution.

7.5 Calculate the equilibrium concentrations of all other species in solution d).

SOLUTION

7.1 $\left[Ca^{2+}\right]\left[C_2O_4^{2-}\right] = K_s$ (1) $\qquad$ $\left[H^+\right]\left[OH^-\right] = K_w$ (2)

$$\frac{\left[H^+\right]\left[HC_2O_4^-\right]}{\left[H_2C_2O_4\right]} = K_{a1} \quad (3) \qquad \frac{\left[H^+\right]\left[C_2O_4^{2-}\right]}{\left[HC_2O_4^-\right]} = K_{a2} \quad (4)$$

7.2 $s = \left[Ca^{2+}\right] = \left[C_2O_4^{2-}\right] + \left[HC_2O_4^-\right] + \left[H_2C_2O_4\right]$ (5)

$C = \left[H^+\right] + \left[HC_2O_4^-\right] + 2\left[H_2C_2O_4\right] - \left[OH^-\right]$ (6)

Equations (5) or (6) may be replaced by

$\left[H^+\right] + 2\left[Ca^{2+}\right] = \left[HC_2O_4^-\right] + 2\left[C_2O_4^{2-}\right] + \left[OH^-\right] + C$ (7)

7.3 The solubility of calcium oxalate monohydrate is 6.7×10^{-3}. (Calculated according to equation (8)).

7.4 Elimination of the concentrations of oxalate species using equations (1), (3), and (4) yields the following expressions for (5) and (6). (The concentration of hydroxide ions can be neglected.)

$$s_2 = K_s + \frac{\left[\mathrm{H}^+\right] K_s}{K_{a2}} + \frac{\left[\mathrm{H}^+\right]^2 K_s}{K_{a1}\, K_{a2}} \tag{8}$$

$$C = \left[\mathrm{H}^+\right] + \frac{\left[\mathrm{H}^+\right] K_s}{s\, K_{a2}} + \frac{2\left[\mathrm{H}^+\right]^2 K_s}{s\, K_{a1}\, K_{a2}} \tag{9}$$

Elimination of *s* from (8) and (9) results in 4th order equation. For this reason, an iterative method is to be preferred. The first approximation is $\left[\mathrm{H}^+\right] = C$. This value of $\left[\mathrm{H}^+\right]$ can be used to calculate:

i) solubility *s* from (8),

ii) the last two terms in (9), which are corrections. Now a new value for $\left[\mathrm{H}^+\right]$ obtained from (9) may be used as a starting value for the next approximation. Two repeated operations give the following value for *s*:

$s = 6.6 \times 10^{-4}$ mol dm^{-3} = 9.6×10^{-2} g dm^{-3}

$\left[\mathrm{H}^+\right] = 9.3 \times 10^{-3}$ mol dm^{-3}

7.5 $\left[\mathrm{Ca}^{2+}\right] = 6.6\times10^{-4}$ mol dm^{-3}

$\left[\mathrm{Cl}^-\right] = 0.010$ mol dm^{-3}

$\left[\mathrm{OH}^-\right] = 1.1\times10^{-12}$ mol dm^{-3}

$\left[\mathrm{C_2O_4^{2-}}\right] = 3.2\times10^{-6}$ mol dm^{-3}

$\left[\mathrm{HC_2O_4^-}\right] = 5.7\times10^{-4}$ mol dm^{-3}

$\left[\mathrm{H_2C_2O_4}\right] = 9.0\times10^{-5}$ mol dm^{-3}

PROBLEM 3

A sample containing a mixture of sodium chloride and potassium chloride weights 25 g. After its dissolution in water 840 ml of $AgNO_3$ solution (c = 0.5 mol dm^{-3}) is added. The precipitate is filtered off and a strip of copper weighing 100.00 g is dipped into the filtrate. After a given time interval the strip weights 101.52 g.

Calculate the mass percent composition of the mixture.

SOLUTION

$A_r(Cu) = 63.5$ $\qquad A_r(Ag) = 108$

$Cu + 2\ AgNO_3 \rightarrow Cu(NO_3)_2 + 2\ Ag$

y $\qquad\qquad\qquad\qquad$ x

x = the quantity of deposited silver

y = the quantity of dissolved copper

$$\frac{63.5}{y} = \frac{2\times 108}{x}$$

x – y = 101.52 – 100 $\qquad$ x = 1.52 + y

$$\frac{63.5}{y} = \frac{2\times 108}{1.52 + x} \qquad y = 0.63 \qquad x = 2.15\ \text{g}\ Ag^+$$

Mass of silver nitrate:

$$\frac{840}{1000} \times 0.5 \times 170 = 71.4\ \text{g}\ AgNO_3$$

$$\frac{170\ \text{g}\ AgNO_3}{108\ \text{g}\ Ag} = \frac{71.4}{x} \qquad x = 45.36\ \text{g}\ Ag^+$$

Silver consumed for participation

45.36 – 2.15 = 43.21 g Ag^+

Total mass of chloride

$$\frac{108\ \text{g Ag}^+}{35.5\ \text{g Cl}^-} = \frac{43.2}{x} \qquad x = 14.2\ \text{g Cl}^-$$

M_r(NaCl) = 58.5 M_r(KCl) = 74.6

x = mass of NaCl in the mixture

y = mass of KCl in the mixture

mass of Cl^- in NaCl: $\dfrac{35.5\ x}{58.5}$

mass of Cl^- in KCl: $\dfrac{35.5\ y}{74.6}$

$$\frac{35.5\ x}{58.5} + \frac{35.5\ y}{74.6} = 14.2$$

$x + y = 25$

x = 17.6 g NaCl 70.4 % NaCl

y = 7.4 g KCl 29.6 % KCl

PROBLEM 3

A weak acid of total concentration 2×10^{-2} M is dissolved in a buffer of pH = 8.8. The anion A^- of this acid is coloured and has a molar decadic absorption coefficient ε of 2.1×10^4 cm^2 mol^{-1}. A layer l of the solution with 1.0 cm thickness absorbs 60 percent of the incident luminous intensity I_o.

3.1 What is the equation relating the extinction to the thickness of the absorbing layer?

3.2 How large is the concentration of the acid anion in the buffer solution?

3.3 How large is the pK_a of the acid?

SOLUTION

3.1 The Lambert-Beer law e.g.:

$$\log (I_o/I) = A = \varepsilon \,.\, c \,.\, l$$

3.2 $\log [(100-60)/100] = - 2.1 \times 10^4 \times [A^-] \times 1$

$[A^-] = 1.895 \times 10^{-5}$ mol cm^{-3} = 1.895×10^{-2} mol dm^{-3}

3.3 According to the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{[A^-]_{eq}}{[HA]_{eq}}$$

and with the total concentration

$[HA]_{tot} = [HA]_{eq} + [A^-]_{eq} = 2 \times 10^{-2}$ mol dm^{-3}

$$8.8 = pK_a + \log \frac{1.895 \times 10^{-2}}{2 \times 10^{-2} - 1.895 \times 10^{-2}}$$

$pK_a = 7.5$

PROBLEM 4

15 cm^3 of a gaseous hydrocarbon C_xH_y are mixed with 120 cm^3 oxygen and ignited. After the reaction the burned gases are shaken with concentrated aqueous KOH solution. A part of the gases is completely absorbed while 67.5 cm^3 gases remain. It has the same temperature and pressure as the original unburned mixture.

4.1 What is the composition of the remaining gas? Explain.

4.2 How large is the change in the amount of substance per mole of a hydrocarbon C_xH_y when this is burned completely?

4.3 What is the chemical formula of the hydrocarbon used for the experiment? Give the steps of the calculation.

SOLUTION

4.1 The remaining gas is oxygen since the burning products CO_2 and H_2O are completely absorbed in concentrated KOH solution.

4.2 The general stoichiometric equation for complete combustion of a hydrocarbon C_xH_y is as follows:

$C_xH_y + (x + y/4)\ O_2 \rightarrow x\ CO_2 + (y/2)\ H_2O$

The change in amount of substance per mole of hydrocarbon is

$[x + (y/2) – (1 + x + y/4)]$ mol $= [(y/4) – 1]$ mol

4.3 The equation of chemical conversion at the experimental condition is as follows:

$15\ C_xH_y + 120\ O_2 \rightarrow 15x\ CO_2 + (15/2)y\ H_2O + [(120 – 15x – (15/4)y]\ O_2$

For the residual oxygen:

(1) $120 /b – 15x – (15/4)y = 67.5$

and for the total balance of amount of substance:

(2) $15x + (15/2)y + 67.5 = 15 + 120 + 15[(y/4) – 1]$

From equation (1) and (2) follows: $x = 2$ and $y = 6$.

The hydrocarbon in question is ethane.

THE SEVENTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
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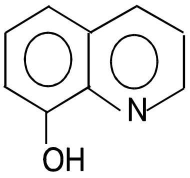
THEORETICAL PROBLEMS

PROBLEM 1

A solution was formed from 0.5284 g of a sample of an alloy containing aluminium. The aluminium was then precipitated as aluminium 8-hydroxyquinolate. The precipitate was separated, dissolved in hydrochloric acid and the 8-hydroxyquinoline formed was titrated with a standard solution of potassium bromate containing potassium bromide. The concentration of the standard potassium bromate solution was 0.0200 M and 17.40 cm^3 of it were required. The resultant product is a dibromo derivative of 8-hydroxyquinoline.

The structural formula of 8-hydroxiquinoline is:



The relative atomic mass of aluminium is 26.98.

Problems:

1.1 Write the balanced equation for the reaction of the aluminium (III) ion with 8-hydroxyquinoline, showing clearly the structure of the products.

1.2 Give the name of the type of compound which is formed during the precipitation.

1.3 Write the balanced equation for the reaction in which bromine is produced.

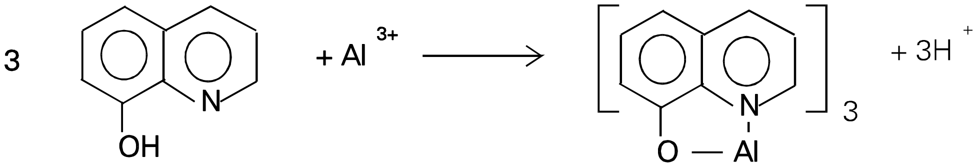
1.4 Write the balanced equation for the reaction of bromine with 8-hydroxyquinoline.

1.5 Calculate the molar ratio of aluminium ions to bromate ions.

1.6 Calculate the percentage by weight of aluminium in the alloy.

SOLUTION

1.1



1.2 Chelate

1.3

$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$

1.4

1.5 As Al $\triangleq$ Al(oxine)$_3$ $\triangleq$ 3 oxine $\triangleq$ 12 Br $\triangleq$ 12 e,

the chemical equivalent of Al equals 26.98/12 = 2.248.

1.6 The percentage of the aluminium in the sample is

$$\%\,Al = \frac{17.40 \times 0.1000 \times 2.248 \times 100}{528.4} = 0.74$$

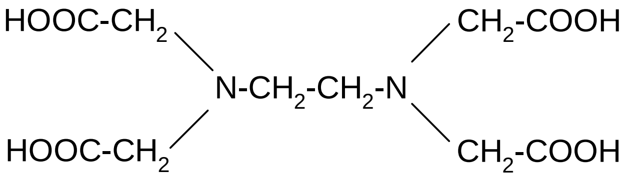
The alloy contains 0.74% of aluminium.

PROBLEM 3

Calcium sulphate is a sparingly soluble compound. Its solubility product is given by:

$K_s(CaSO_4) = [Ca^{2+}][SO_4^{2-}] = 6.1 \times 10^{-5}$

Ethylenediaminetetraacetic acid (EDTA) has the formula $C_{10}H_{16}N_2O_8$ and the structure:



The anion of this acid, $C_{10}H_{12}N_2O_8^{4-}$, forms a stable complex $CaC_{10}H_{12}N_2O_8^{2-}$ with calcium ions. The stability constant of this complex ion is given by:

$$K = \frac{[CaC_{10}H_{12}N_2O_8^{2-}]}{[Ca^{2+}][C_{10}H_{12}N_2O_8^{4-}]} = 1.0 \times 10^{11}$$

EDTA is completely dissociated in strongly alkaline solution. The equation for this dissociation is:

$C_{10}H_{16}N_2O_8 \rightarrow 4\ H^+ + C_{10}H_{12}N_2O_8^{4-}$

Problems:

3.1 Calculate the concentration of calcium ions in a saturated solution of calcium sulphate.

3.2 Calculate the concentration of free Ca^{2+} cations in a solution of 0.1 M $Na_2(CaC_{10}H_{12}N_2O_8)$. You should ignore any protonation of the ligand.

3.3 How many moles of calcium sulphate will dissolve in 1 litre of a strongly alkaline solution of 0.1 M $Na_4C_{10}H_{12}N_2O_8$?

What would be the concentrations of the calcium and sulphate ions in the resulting solution?

3.4 Suggest a structure for the complex ion $[CaC_{10}H_{12}N_2O_8]^{2-}$ assuming that it is approximately octahedral.

3.5 Is the structure you have suggested in 4) optically active?

If your answer is "yes" then draw the structure of the other optical isomer enantiomer).

3.6 Explain why the complexes formed by the anion $C_{10}H_{12}N_2O_8^{4-}$ are exceptionally table.

SOLUTION

3.1 [Ca^{2+}] = 7.8×10^{-3} mol dm^{-3}

3.2 [Ca^{2+}] = 1.0×10^{-6} mol dm^{-3}

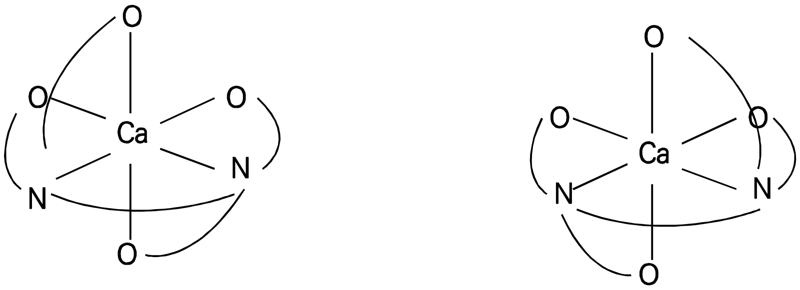
3.3 The $CaSO_4$ amount dissolved is 0.1 mol.

[SO_4^{2-}] = 0.10 mol dm^{-3}.

[Ca^{2+}] = 6.1×10^{-4} mol dm^{-3}

3.4 + **3.5**

The complex is optically active. The structures of both enantiomers are



3.6 The high number of the chelate rings. Other factors also contribute to the complex ability, e.g. the character of the donor atoms, the magnitude and distribution of the charges in the anion, etc.

PROBLEM 8

The following reaction scheme represents part of anaerobic degradation of saccharides, i.e. the glycolysis, involving equilibrium constants K_1 and K_2:

glucose-1-phosphate $\rightleftharpoons$ glucose-6-phosphate $K_1 = 19$

glucose-6-phosphate $\rightleftharpoons$ fructose-6-phosphate $K_2 = 0.50$

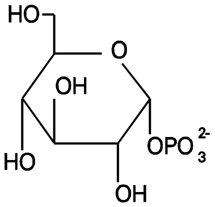
Problems:

8.1 Give the structural formulae for all the three reactants (compounds) that are mutually interconverted, i.e. α-D-glucose-1-phosphate, α-D-glucose-6-phosphate and α-D-fructose-6-phosphate.

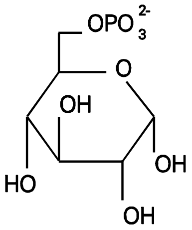
8.2 In the beginning of the reaction the reaction mixture contained 1 mmol of glucose-6-phosphate. Calculate the amounts of glucose-6-phosphate, glucose-1-phosphate and fructose-6-phosphate in the mixture at equilibrium. (As the reaction take place in a constant volume, the ratio of the amounts of substances equals that of their concentrations.)

SOLUTION

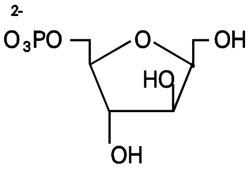
8.1 α-D-glucose-1-phosphate



α-D-glucose-6-phosphate



α-D-fructose-6-phosphate



8.2 It holds for the equilibrium constant of the successive reactions, that

$$\frac{\text{Fru-6-P}}{\text{Glc-1-P}} = 19 \times 0.5 = 9.5 \qquad \text{(i)}$$

If y mmoles of Glc-6-phosphate are converted into the same number of Glc-1-phosphate and another x mmoles of Glc-6-phosphate are converted into the same number of mmoles of Fru-6-phosphate, then (1 – x – y) mmoles of Glc-6-phosphate remain in the reaction mixture at equilibrium. It follows from relationship (i) that

Glc-1-phosphate = y x/y = 9.5

Fru-6-phosphate = x x = 9.5 y

After substituting,

Glc-6-phosphate = 1 – x – y = 1 – 10.5y,

it is possible to write for the reaction mixture at equilibrium that

$$\frac{\text{Glc-6-P}}{\text{Glc-1-P}} = \frac{1 - 10.5y}{y} = 19 \qquad 1 - 10.5y = 19\,y$$

y = 1/29.5 = 0.034 mmoles Glc-1-phoshate

It is further calculated that

x = 9.5y = 9.5 $\times$ 0.034 or 9.5/29.5 = 0.322 mmoles of Fru-6-phosphate

1 – x – y = 1 – 0.322 – 0.034 = 0.644 mmoles of Glc-6-phosphate

At equilibrium the reaction mixture contains 0.034 mmoles Glc-1-phosphate, 0.644 mmoles Glc-6-phosphate and 0.322 mmoles Fru-6-phosphate.

PROBLEM 2

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 cm^3 of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 cm^3 and 20.0 cm^3 of it are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 cm^3. The pH at the end-point is 10.00.

Problems:

2.1 Calculate the percentage distribution by moles of all protonated $H_nPO_4^{n-3}$ species at the end-point.

2.2 What is the stoichiometric formula of the salt?

The cumulative protonation constants are given by

$$\beta_n = \frac{[H_nPO_4^{n-3}]}{[PO_4^{3-}][H^+]^n}$$

where $\log\beta_1 = 11.70$; $\log\beta_2 = 18.6$; $\log\beta_3 = 20.6$.

The relative atomic masses are: Na = 23.0; P = 31.0; H = 1.0; O = 16.0.

SOLUTION

2.1 $[H_3PO_4] + [HPO_4^{2-}] + [H_2PO_4^-] + [PO_4^{3-}] = T_{konst}$; $[H^+] = 10^{-10}$ mol dm^{-3}

$[H_3PO_4] = 1$ mol dm^{-3}

$[HPO_4^{2-}] = \beta_1[PO_4^{3-}][H^+] = 1.25 \times 10^{10}$ mol dm^{-3} = 97.97 %

$[H_2PO_4^-] = \beta_2[PO_4^{3-}][H^+]^2 = 1 \times 10^8$ mol dm^{-3} = 0.078 %

$[PO_4^{3-}] = (\beta_3 [H^+]^3)^{-1} = 2.5 \times 10^9$ mol dm^{-3} = 1.955 %

2.2 A general formula of the salt: $Na_{3-n}(H_nPO_4) \times m\ H_2O$ (n = 0,1,2)

The titrated solution contains 100 mg (y mol) of the salt and 1.00 mmol of sulphuric acid. The reacted protons (in mmol) can be calculated using the results of a):

$2 + (n - 0.9797 - 2 \times 0.00078)\ y = 2.653$

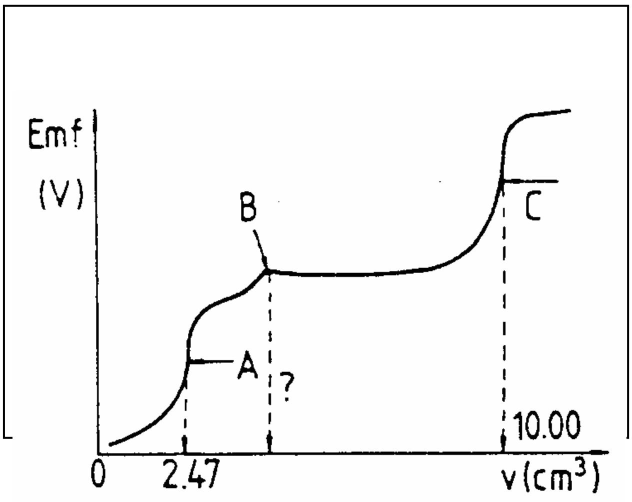
Since y = 100/*M* (in mmol) but $M \geq 120$ g mol^{-1}, the only real solution is n = 2.

Therefore M = 156 g mol^{-1}, m is (156-120)/18 = 2 ⇒ $\underline{NaH_2PO_4 \cdot 2\ H_2O}$

PROBLEM 3

25.00 cm^3 of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25 °C using a silver electrode and a normal calomel half-cell with KNO_3 - salt bridge. The protonation of cyanide ions is negligible. The potentiometric curve obtained (emf (V)) vs. burette readings (in cm^3) is shown in Fig. 1.

Fig. 1



3.1 The end points of the reactions taking place during the titration, are marked with A, B and C. Write the balanced ionic equation for each reaction.

3.2 What volume of the titrant is required to reach point B?

3.3 Calculate the concentrations of KCl and KCN (in mol dm^{-3}) in the sample solution.

3.4 Calculate the emf readings at the points A and C in volts.

3.5 What is the molar ratio Cl^-/CN^- in the solution and in the precipitate at point C?

Data:

$E^o(Ag^+/Ag) = 0.800$ V

E^o(Calomel) = 0.285 V

$K_{sp}(AgCN) = 10^{-15.8}$

$K_{sp}(AgCl) = 10^{-9.75}$

$$\beta_2 = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = 10^{21.1}$$

SOLUTION

3.1 β_2 indicates that the complexation of Ag^+ with CN^- occurs easily. Thus A denotes the point where all Ag^+ is present in the complex form, having a higher potential than Ag^+, B shows the point where the precipitation of AgCN starts, thus leading to a constant Ag^+ concentration until all CN^- is precipitated. Now at point C the precipitation of the more soluble AgCl begins:

A: $Ag^+ + 2\ CN^- \rightarrow [Ag(CN)_2]^-$

B: $[Ag(CN)_2]^- + Ag^+ \rightarrow 2\ AgCN \downarrow$

C: $Ag^+ + Cl^- \rightarrow AgCl \downarrow$

3.2 $2 \times 2.47\ cm^3 = \underline{4.94\ cm^3}$

3.3 $[CN^-] = (4.94 \times 0.1 \times 40)/1000\ mol\ dm^{-3} = 1.98 \times 10^{-2}\ mol\ dm^{-3}$

$[Cl^-] = ((10 - 4.94) \times 0.1 \times 40)/1000\ mol\ dm^{-3} = 2.02 \times 10^{-2}\ mol\ dm^{-3}$

3.4 For the system Ag/Ag^+ at point A: $E = E_o + 0.059\ \log[Ag^+]$.

The following equations are derived from the equilibrium conditions:

$$[Ag^+] = \frac{[Ag(CN^-)_2]}{[CN^-]^2\ \beta_2}$$

$$[Ag^+] + [Ag(CN^-)_2] = \frac{2.47 \times 0.1}{25 + 2.47}$$

$$[CN^-] = 2\ [Ag^+]$$

It yields an equation of third degree in $[Ag^+]$:

$$4\beta_2[Ag^+]^3 + [Ag(CN^-)_2] = 0$$

$[Ag(CN^-)_2]$ can be assumed to be $(2.47 \times 0.1) / 27.47\ mol\ dm^{-3}$, and therefore $[Ag^+]$ equals $1.213 \times 10^{-8}\ mol\ dm^{-3}$.

The emf will be: $E = 0.8 + 0.059\ \log[Ag^+] - 0.285 = \underline{0.048\ V}$

At point C: $[Ag+] = \sqrt{K_{sp}(AgCl)} = 1.333 \times 10^{-5}$ and

$E = 0.8 + 0.059\ \log[Ag^+] - 0.285 = \underline{0.227\ V}$

3.5 Since both AgCN and AgCl are present as the precipitate, the solution must be saturated:

In the solution: $[Cl^-]/[CN^-] = K_{sp}(AgCl)/K_{sp}(AgCN) = 10^{6.05} = \underline{1.222 \times 10^6}$

In the precipitate: $n(AgCl) / n(AgCN) = 2.02 / 1.98 = \underline{1.02}$

PROBLEM 4

Chloride ions are analytically determined by precipitating them with silver nitrate. The precipitate is undergoing decomposition in presence of light and forms elemental silver and chlorine. In aqueous solution the latter disproportionates to chlorate(V) and chloride. With excess of silver ions, the chloride ions formed are precipitated whereas chlorate(V) ions are not.

4.1 Write the balanced equations of the reactions mentioned above.

4.2 The gravimetric determination yielded a precipitate of which 12 % by mass was decomposed by light. Determine the size and direction of the error caused by this decomposition.

4.3 Consider a solution containing two weak acids HA and HL, 0.020 molar and 0.010 molar solutions, respectively. The acid constants are 1×10^{-4} for HA and 1×10^{-7} for HL. Calculate the pH of the solution.

4.4 M forms a complex ML with the acid H_2L with the formation constant K_1. The solution contains another metal ion N that forms a complex NHL with the acid H_2L. Determine the conditional equilibrium constant, K'_1 for the complex ML in terms of $[H^+]$ and K values.

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K_{1'} = \frac{[ML]}{[M'][L']}$$

[M'] = total concentration of M not bound in ML

[L'] = the sum of the concentrations of all species containing L except ML

In addition to K_1, the acid constants K_{a1} and K_{a2} of H_2L as well as the formation constant K_{NHL} of NHL are known.

$$K_{NHL} = \frac{[NHL]}{[N]\,[L]\,[H^+]}$$

You may assume that the equilibrium concentration $[H^+]$ and [N] are known, too.

SOLUTION

4.1 $Ag^+ + Cl^- \rightarrow AgCl\downarrow$

$2\,AgCl \rightarrow 2\,Ag + Cl_2$

$3\,Cl_2 + 3\,H_2O \rightarrow ClO_3^- + 5\,Cl^- + 6\,H^+$

Total:

$6\,AgCl + 3\,H_2O \rightarrow 6\,Ag + ClO_3^- + 5\,Cl^- + 6\,H^+$ or

$3\,Cl_2 + 5\,Ag^+ + 3\,H_2O \rightarrow ClO_3^- + 5\,AgCl + 6\,H^+$

4.2 From 100 g AgCl 12 g decompose and 88 g remain. 12 g equals 0.0837 mol and therefore, 0.04185 mol Cl_2 are liberated. Out of that (12 × 107.9) / 143.3 = 9.03 g Ag remain in the precipitate. 5/6 × 0.837 mol AgCl are newly formed (= 10.0 g), so that the total mass of precipitate (A) yields:

A = 88 g + 9.03 g + 10.0 g = <u>107.03 g</u>; relative error = <u>7.03 %</u>

4.3 $[H^+] = [A^-] + [L^-] + [OH^-]$

$[HA] + [A^-] = 0.02$ mol dm^{-3} $pK(HA) = pH + p[A\text{-}] - p[HA] = 4$

$[HL] + [L^-] = 0.01$ mol dm^{-3} $pK(HL) = pH + p[L\text{-}] - p[HL] = 7$

For problems like these, where no formal algebraic solution is found, only simplifications lead to a good approximation of the desired result, e.g.

1. $[H^+] = [A^-]$ (since HA is a much stronger acid than HL then $[A^-] \gg [L^-] + [OH^-]$)

   $[H^+]^2 + K_{(HA)}[H^+] - K_{(HA)}0.02 = 0$

   $[H^+] = 1.365 \times 10^{-3}$ mol dm^{-3}

   pH = <u>2.865</u>

2. Linear combination of the equations

   $$[H+] = K_{(HA)}\,\frac{[HA]}{[A^-]} = K_{(HL)}\,\frac{[HL]}{[L^-]};$$

   $[HA] = 0.02 - [A^-]$;

   $[HL] = 0.01 - [L^-]$;

   $[H^+] = [A^-] + [L^-] + [OH^-]$

   yields:

$$[A] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}}$$

$$[L] = \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}}$$

$$[H^+] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}} + \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}} + \frac{K_w}{[H^+]}$$

The equation above can only be solved by numerical approximation methods. The result is pH = 2.865. We see that it is not necessary to consider all equations. Simplifications can be made here without loss of accuracy. Obviously it is quite difficult to see the effects of a simplification - but being aware of the fact that already the so-called exact solution is not really an exact one (e.g. activities are not being considered), simple assumption often lead to a very accurate result.

4.4

$$K_{1'} = \frac{[ML]}{[M]([L] + [HL] + [NHL] + [H_2L])} = \frac{K_1 [L]}{([L] + [HL] + [NHL] + [H_2L])}$$

$$[HL] = \frac{K_{a1} [H_2L]}{[H]}$$

$$[HL] = \frac{[L]\,[H]}{K_{a2}}$$

$$[L] = \frac{K_{a2}\,[HL]}{[H]} = \frac{K_{a1} K_{a2}\,[H_2L]}{[H]^2}$$

$$[NHL] = K_{NHL}\,[N]\,[L]\,[H]$$

$$K_{1'} = \frac{K_1}{\left[1 + \frac{[H]}{K_{a1}} + \frac{[H]^2}{K_{a1}\,K_{a2}} + K_{NHL}[N][H]\right]}$$

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THEORETICAL PROBLEMS

PROBLEM 1

To determine the solubility product of copper(II) iodate, $Cu(IO_3)_2$, by iodometric titration in an acidic solution (25 °C) 30.00 cm^3 of a 0.100 molar sodium thiosulphate solution are needed to titrate 20.00 cm^3 of a saturated aqueous solution $Cu(IO_3)_2$.

1.1 Write the sequence of balanced equations for the above described reactions.

1.2 Calculate the initial concentration of Cu^{2+} and the solubility product of copper(II) iodate. Activity coefficients can be neglected.

SOLUTION

1.1 $2\ Cu^{2+} + 4\ IO_3^- + 24\ I^- + 24\ H^+ \rightarrow 2\ CuI + 13\ I_2 + 12\ H_2O$ (1)

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$ (2)

1.2 From (2):

$n(S_2O_3^{2-}) = c\ V = 0{,}100\ \text{mol dm}^{-3} \times 0{,}03000\ \text{dm}^3 = 3.00\times10^{-3}\ \text{mol}$

From (2) and (1):

$n(I_2) = 1.50\times10^{-3}\ \text{mol}$

$$n(Cu^{2+}) = \frac{1.50\times10^{-3}\ \text{mol}}{13} \times 2 = 2.31\times10^{-4}\ \text{mol}$$

$$c(Cu^{2+}) = \frac{2.31\times10^{-4}\ \text{mol}}{0.02000\ \text{dm}^3} = 1.15\times10^{-2}\ \text{mol}$$

$[Cu^{2+}] = 1.15\times10^{-2}$

$[IO_3^-] = 2\,[Cu^{2+}]$

$K_{sp} = [Cu^{2+}]\,[IO_3^-]^2 = 4\,[Cu^{2+}]^3 = 4 \times (1.15\times10^{-2})^3 = 6.08\times10^{-6}$

PROBLEM 3

Sulphur dioxide is removed from waste gases of coal power stations by washing with aqueous suspensions of calcium carbonate or calcium hydroxide. The residue formed is recovered.

3.1 Write all reactions as balanced equations.

3.2 How many kilograms of calcium carbonate are daily consumed to remove 95 % of the sulphur dioxide if 10000 m^3/h of waste gas (corrected to 0 °C and standard pressure) containing 0.15 % sulphur dioxide by volume are processed? How many kilograms of gypsum are recovered thereby?

3.3 Assuming that the sulphur dioxide is not being removed and equally spread in an atmospheric liquid water pool of 5000 m^3 and fully returned on earth as rain, what is the expected pH of the condensed water?

3.4 If a sodium sulphite solution is used for absorption, sulphur dioxide and the sulphite solution can be recovered. Write down the balanced equations and point out possible pathways to increase the recovery of sulphur dioxide from an aqueous solution.

Note:

Protolysis of sulphur dioxide in aqueous solutions can be described by the first step dissociation of sulphurous acid. The dissociation constant $K_{a,1}(H_2SO_3) = 10^{-2.25}$.

Assume ideal gases and a constant temperature of 0 °C at standard pressure.

$M(CaCO_3) = 100 \text{ g mol}^{-1}$; $M(CaSO_4) = 172 \text{ g mol}^{-1}$.

SOLUTION

3.1 $SO_2 + CaCO_3 + ½\ O_2 + 2\ H_2O \rightarrow CaSO_4 . 2\ H_2O + CO_2$

$SO_2 + Ca(OH)_2 + ½\ O_2 + H_2O \rightarrow CaSO_4 . 2\ H_2O$

3.2 Under given conditions:

$n(SO_2)/h = v(SO_2/h) / V = 669.34 \text{ mol h}^{-1}$

$m(CaCO_3/d) = n(SO_2/h) \times M(CaCO_3) \times 24 \text{ h} \cdot \text{d}^{-1} \times 0.95 = 1.53 \times 10^3 \text{ kg/d}$

$$m(CaSO_4 \,.\, 2\,H_2O) = \frac{M(CaSO_4\,.\,2\,H_2O)}{M(CaCO_3)} \times m(CaCO_3)\,/\,d\; = 2.63\times10^3\ \text{kg/d}$$

3.3 $pH = -\log[H_3O^+]$; $K_a = \dfrac{[H_3O^+]^2}{[SO_2] - [H_3O^+]}$

$$[H_3O^+]_{1/2} = -\frac{K_a}{2} \pm \sqrt{\frac{K_a^2}{4} + K_A\,[SO_2]}$$

Solving for $[H_3O^+]$:

If $[SO_2] = n(SO_2)\,/\,V = 1.34\times10^{-4}$ and $K_a = 1\times10^{-2.25}$, then $[H_3O^+] = 1.32\times10^{-4}$ and $pH = 3.88$

3.4 $SO_2 + Na_2SO_3 + H_2O \rightarrow 2\,NaHSO_3$

Possibilities to increase the recovery of SO_2 are: temperature rise, reduced pressure, lower *pH*-value.

PROBLEM 2

IONIC SOLUTIONS – AQUEOUS SOLUTIONS OF COPPER SALTS

This part is about the acidity of the hydrated Cu^{2+} ion and the precipitation of the hydroxide.

Consider a 1.00×10^{-2} mol dm^{-3} solution of copper(II) nitrate. The *pH* of this solution is 4.65.

2.1 Give the equation for the formation of the conjugate base of the hydrated Cu^{2+} ion.

2.2 Calculate the pK_a of the corresponding acid-base pair.

The solubility product of copper(II) hydroxide is $K_{sp} = 1 \times 10^{-20}$.

2.3 At what *pH* value hydroxide $Cu(OH)_2$ precipitates from the solution under consideration? Justify your calculation showing that the conjugate base of this hydrated Cu^{2+} ion is present in negligible quantity.

Disproportionation of copper(I) ions

The Cu^+ ion is involved in two redox couples:

Couple 1: $Cu^+ + e^- \rightleftharpoons Cu$

Standard electrode potential $E_1^0 = +\ 0.52$ V

Couple 2: $Cu^{2+} + e^- \rightleftharpoons Cu^+$

Standard electrode potential $E_2^0 = +\ 0.16$ V

2.4 Write down the equation for the disproportionation of copper(I) ions and calculate the corresponding equilibrium constant.

2.5 Calculate the composition of the solution (in mol dm^{-3}) obtained on dissolving 1.00×10^{-2} mol of copper(I) in 1.0 dm^3 of water.

2.6 Apart from Cu^+ ions, name two chemical species which also disproportionate in aqueous solution; write down the equations and describe the experimental conditions under which disproportionation is observed.

Consider the stability of copper(I) oxide, Cu_2O, in contact with a 1.00×10^{-2} mol dm^{-3} solution of Cu^{2+} ions. The solubility product of copper(I) oxide is $K_{sp} = [Cu^+][OH^-] = 1\times10^{-15}$

2.7 Calculate the pH value at which Cu_2O becomes stable. Quote a simple experiment allowing the observation of the precipitation of Cu_2O.

Complex formation involving Cu^+ and Cu^{2+} ions

2.8 The dissociation constant of the complex ion $[Cu(NH_3)_2]^+$ is $K_D = 1\times10^{-11}$. Calculate the standard electrode potential of the couple:

$$[Cu(NH_3)_2]^+ + e^- \rightleftarrows Cu + 2\ NH_3$$

2.9 The standard electrode potential of the couple

$$[Cu(NH_3)_4]^{2+} + 2\ e^- \rightleftarrows Cu + 4\ NH_3$$

$E_3^0 = -\ 0,02$ V.

Calculate the dissociation constant for the complex ion $[Cu(NH_3)_4]^{2+}$.

2.10 Deduce from it the standard electrode potential of the couple:

$$[Cu(NH_3)_4]^{2+} + e^- \rightleftarrows [Cu(NH_3)_2]^+ + 2\ NH_3$$

Does the disproportionation of the cation $[Cu(NH_3)_2]^+$ take place?

SOLUTION

2.1 $[Cu(H_2O)_4]^{2+} + H_2O \rightarrow H_3O^+ + [Cu(OH)(H_2O)_3]^+$

2.2 $$K_a = \frac{[H_3O^+]\left[[Cu(OH)(H_2O)_3]^+\right]}{\left[[Cu(H_2O)_4]^{2+}\right]} = \frac{[H_3O^+]^2}{\left[[Cu(H_2O)_4]^{2+}\right]} = \frac{(2.24\times10^{-5})^2}{1\times10^{-2}} = 5.01\times10^{-8}$$

$pK_a = 7.30$

2.3 $[Cu^{2+}][OH^-]^2 = 1\times10^{-20}$; $[Cu^{2+}] = 1\times10^{-2}$ $\Rightarrow$ $[OH^-] = 1\times10^{-9}$; $\underline{pH = 5}$

$$\left[[Cu(OH)(H_2O)_3]^+\right] : \left[[Cu(H_2O)_4]^{2+}\right] = K_a : 10^{-pH} = 1\times10^{-7.3} : 1\times10^{-5} = 1 : 200$$

2.4 $2\ Cu^+ \rightarrow Cu^{2+} + Cu$

$$K = \frac{[Cu^{2+}]}{[Cu^+]^2}$$

$0.52 - 0.16 = 0.059 \log K$ (Nernst equation) $\Rightarrow K = 1\times10^6$

2.5 At equilibrium: $[Cu^+] + 2\,[Cu^{2+}] = 1\times10^{-2}$ and $[Cu^{2+}] = 1\times10^6\,[Cu^+]$ so that the following equation is obtained:

$2\times10^6\,[Cu^+]^2 + [Cu^+] - 1\times10^{-2} = 0$

with the solution

$[Cu^+] = \underline{7.07\times10^{-5}}$ and $[Cu^{2+}] = \underline{4.96\times10^{-3}}$.

2.6 Other disproportionation reactions:

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ (catalyzed by $KMnO_4$, Fe^{3+} etc.)

$Cl_2 + OH^- \rightarrow HCl + ClO^-$ (basic conditions)

2.7 $Cu_2O + 2\ H_3O^+ + 2\ e^- \rightarrow 2\ Cu + 3\ H_2O$ $\qquad [Cu^+] = \dfrac{1\cdot10^{-15}}{[OH^-]}$

$$E_1 = 0.52 + \frac{0.059}{2}\log\left([Cu^+][H_3O^+]^2\right) = 0.49 - 0.0885\,pH$$

$2\ Cu^{2+} + 3\ H_2O + 2\ e^- \rightarrow Cu_2O + 2\ H_3O^+$

$$E_2 = 0.16 + \frac{0.059}{2}\log\frac{1\times10^{-4}}{[Cu^+][H_3O^+]^2} = 0.07 + 0.0885\,pH$$

Cu_2O is stable when $E_2 > E_1$ i.e. $0.42 < 0.177$ pH, or pH > 2.4

Cu_2O can be obtained by the reduction of Cu^{2+} in acid or basic media, e.g. by Fehling's solution or reducing sugars.

2.8 $[Cu(NH_3)_2]^+ \rightleftharpoons Cu^+ + 2\ NH_3$

$$K_D = \frac{[Cu^+]\,[NH_3]^2}{\left[[Cu(NH_3)_2{}^+]\right]} = 1\times10^{-11}$$

Knowing $E_0(Cu^+/Cu) = 0.52$ V, the $E^0([Cu(NH_3)_2]^+ / Cu^+)$ becomes:

$E_{f1} = 0.52 - 0.06\,pK_D = -\,\underline{0.14\ V}$

2.9 The standard *emf* of a Cu^{2+}/Cu cell is thus: E^0 = (0.5 + 0.16)/2 = 0.33 V and $E_3^0 = 0.33 - 0.03\ pK_2$.

Thereout: $pK_2 = (0.33 - E_3^0) / 0.03 = (0.33 - (-0.02)) / 0.03 = \underline{12}$

$[Cu(NH_3)_4]^{2+} + 2\,e^- \rightarrow Cu + 4\,NH_3 \quad E_0 = -0.02$ V

$[Cu(NH_3)_2]^{+} + e^- \rightarrow Cu + 2\,NH_3 \quad E_0 = -0.14$ V

$[Cu(NH_3)_4]^{2+} + e^- \rightarrow [Cu(NH_3)_2]^{+} + 2\,NH_3$

Since only ΔG^0 is additive and from $\Delta G^0 = -n\,F\,E^0$ it follows:

$E_{f2} = 2 \times (-0.02) - (-0.14) = 0.10$ V

2.10 $[Cu(NH_3)_2]^{+} + e^- \rightarrow Cu + 2\,NH_3 \qquad E_{f1} = -0.14$ V

$[Cu(NH_3)_4]^{2+} + e^- \rightarrow [Cu(NH_3)_2]^{+} + 2\,NH_3 \qquad E_{f2} = 0.10$ V

Since $E_{f1} < E_{f2}$ the $[Cu(NH_3)_2]^{+}$ ion doesn't disproportionate (the *emf* would be – 0.14 – 0.10 = – 0.24 V)

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THEORETICAL PROBLEMS

PROBLEM 1

1.1 Show that 0.1 mol of Tl_2S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.

1.2 Show that 0.1 CuS dissolves in a 1 M HNO_3 but not in a 1 M HCl solution.

Information:

Assume that Cu^{2+} ions do not form stable complexes with chloride ions in aqueous solutions.

$E^0(S/S^{2-}) = -0.48$ V $\quad$ $E^0(NO_3^- / NO_{(aq)}) = 0.96$ V

$pK_a(H_2S) = 7$ $\quad$ $pK_a(HS^-) = 13$

$K_{sp}(Tl_2S) = 1\times10^{-20}$ $\quad$ $K_{sp}(CuS) = 1\times10^{-35}$

Solubility of NO in water (298 K): 2.53×10^{-2} mol dm^{-3}

Solubility of H_2S in water (298 K): 0.1 mol dm^{-3}

$R = 8.314$ J K^{-1} mol^{-1} $\quad$ $F = 96\,487$ C mol^{-1}

SOLUTION

1.1 Solubility condition: $[Tl^+]^2\,[S^{2-}] \le 1\times10^{-20}$

$[Tl^+] = c(Tl^+) = 0.2$ mol dm^{-3}

$$c(S^{2-}) = [S^{2-}] + [HS^-] + [H_2S] = [S^{2-}]\left(1+\frac{[H^+]}{K_2}+\frac{[H^+]^2}{K_1K_2}\right) = 0.1 \text{ mol dm}^{-3}$$

$$[S^{2-}] = \frac{0.1}{1+\frac{[H^+]}{K_2}+\frac{[H^+]^2}{K_1 K_2}} \Rightarrow$$

For a strong monoprotic acid (1 mol dm^{-3}) and $[H^+] \approx 1$.

Then

$$1 + 10^{13}\,[H^+] \ll 10^{20}\,[H^+]^2 \qquad \text{and} \qquad [S^{2-}] \approx \frac{0.1}{1\times 10^{20}}$$

$$[Tl^+]^2\,[S^{2-}] = \frac{(0.2)^2 \times 0.1}{1\times 10^{20}} = 4\times 10^{-23} < K_s(Tl_2S)$$

Thus, 0.1 mol of Tl_2S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.

1.2

- Dissolving CuS in 1 M solution HCl (non-oxidizing and non-complexing acid):

  c(Cu^{2+}) = 0.1 mol dm^{-3}

  $[Cu^{2+}] = 0.1$

  $c(S^{2-})$ = 0.1 mol dm^{-3}

  Similarly as in part (1.1):

  $$[S^{2-}] = \frac{0.1}{1+\frac{[H^+]}{K_2}+\frac{[H^+]^2}{K_1 K_2}}$$

  $$[S^{2-}] \approx \frac{0.1}{1\times 10^{20}}$$

  $$[Cu^{2+}]\,[S^{2-}] = \frac{(0.1)^2 \times 0.1}{1\times 10^{20}} \approx 1\times 10^{-23} > K_s(CuS)$$

  Conclusion: 0.1 mol CuS does not dissolve in 1 M solution HCl.

- When dissolving 0.1 mol CuS in 1 M HNO_3 an additional redox process occurs: the oxidation of S^{2-} to S.

  $$2\,NO_3^- + 8\,H^+ + 3\,S^{2-} \rightarrow 3\,S + 2\,NO + 4\,H_2O$$

  The emf of this reaction is $\Delta E = E_1^0 - E_2^0$ = (0.96 + 0.48) = <u>1.44 V</u>

  $$\log K = \frac{\Delta G}{RT} = \frac{n\,F}{R\,T}\,\Delta E = \frac{n_1 n_2 (E_1^o - E_2^o)}{0.0591} \cong 144 \qquad K = 1\times 10^{144}$$

The equilibrium constant of this process can also be written in the form:

$$K = \frac{[NO]^2}{[NO_3^-]^2\,[H^+]^8\,[S^{2-}]^3}$$

From the above equilibrium follows that $[S^{2-}] = \sqrt[3]{\frac{K\,[NO_3^-]^2\,[H^+]^8}{[NO]^2}}$

Since $[NO_3^-] = [H^+] = 1$

$$[S^{2-}] = \sqrt[3]{\frac{K}{[NO]^2}}$$

$c_{CuS} = [S] + [H_2S] + [HS^-] + [S^{2-}]$

$$[S^{2-}] = \frac{c_{CuS}}{1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1\,K_2} + \sqrt[3]{\frac{K}{[NO]^2}}}$$

However

$$1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1\,K_2} \ll \sqrt[3]{\frac{K}{[NO]^2}} = \sqrt[3]{\frac{1\times10^{144}}{(0.0253)^2}} = 1.16\times10^{49}$$

$$[S^{2-}] = \frac{0.1}{1.16\times10^{49}} = 8.62\times10^{-51}$$

$[Cu^{2+}]\,[S^{2-}] = 0.1 \times 8.62\times10^{-51} = 8.62\times10^{-52} \ll K_{sp}(CuS)$ $(= 1\times10^{-35})$

Conclusion: CuS dissolves in 1 M solution of HNO_3.

PROBLEM 3

Type II electrodes that are made of a metal covered with a sparingly soluble salt of the metal are dipped into a soluble salt solution containing an anion of the sparingly soluble salt. The silver/silver chloride (Ag, AgCl/Cl$^-$) and the calomel electrode (Hg, Hg_2Cl_2/Cl$^-$) are examples of such electrodes. The standard emf of a cell built of those electrodes (–) Ag,AgCl/Cl$^-$ || Hg_2Cl_2/Hg (+) is $E^0 = 0.0455$ V at $T = 298$ K. The temperature coefficient for this cell is $dE^0/dT = 3.38\times10^{-4}$ V K^{-1}.

3.1 Give the equations of the reactions taking place at both the cell electrodes and the overall cell reaction.

3.2 Calculate the Gibbs free energy change (ΔG^0) for the process taking place in the cell at 298 K. What does its sign imply?

3.3 Calculate the enthalpy change for the process taking place at 298 K.

$\Delta S = n\,F\,\Delta E/\Delta T$.

3.4 Knowing the standard potential of Ag/Ag$^+$ electrode is $E^0 = 0.799$ V and the solubility product of AgCl $K_{sp} = 1.73\times10^{-10}$, calculate the standard electrode potential value of the silver/silver chloride electrode. Derive an expression showing the dependence between E^0(Ag/Ag$^+$) and E^0(Ag, AgCl/Cl$^-$).

3.5 Calculate the solubility product of Hg_2Cl_2 knowing that the standard potential of the calomel electrode is $E^0 = 0.798$ V.

$F = 96487$ C mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}, $T = 298$ K

SOLUTION

3.1 Reduction (calomel electrode (+)): $1/2\ Hg_2Cl_2 + e^- \rightarrow Hg + Cl^-$

Oxidation (silver/silver chloride electrode (-)) $Ag + Cl^- \rightarrow AgCl + e^-$

Summary reaction: $Ag + 1/2\ Hg_2Cl_2 \rightarrow Hg + AgCl$

3.2 $\Delta G^o = -n\,F\,E^0 = -96497\ \text{C mol}^{-1} \times 0.0455\ \text{V} = -4.39\ \text{kJ mol}^{-1}$;

Since ΔG^o is negative, the reaction is spontaneous.

3.3 The change of enthalpy is related to the Gibbs-Helmholtz equation:

$$\Delta H = \Delta G + T\Delta S \;=\; -\,n\,F\,E \;+\; T\,n\,F\;\left(\frac{\Delta E^0}{\Delta t}\right) = -\,n\,F\left(E \;-\; T\;\left(\frac{\Delta E^0}{\Delta t}\right)\right) =$$

$$= \;-\,96487\text{ C mol}^{-1}\,(0.0455\text{ V} - 298\text{ K}\times 3.38\times10^{-4}\text{ V K}^{-1}) \;=\; 5.36\text{ kJ mol}^{-1}$$

3.4 For the Ag│ Ag$^+$ electrode: $E = E^o + 0.0591\log[\text{Ag}^+]$

For the Ag,AgCl│ Cl$^-$ electrode [Ag$^+$] is determined by the solubility product:

$$[\text{Ag}^+] = \frac{K_{sp}}{\left[\text{Cl}^-\right]}$$

$$E^o(\text{Ag, AgCl}│\text{ Cl}^-) = E^o\,(\text{Ag}│\text{ Ag}^+) + \;0.0591\log K_{sp} = 0.799 - 0.577 = 0.222\text{ V}$$

3.5 $E^o(\text{Hg, Hg}_2\text{Cl}_2│\text{ Cl}^-) \;= E^o\,(\text{Hg}│\text{ Hg}^{2+}) \;+\; \dfrac{0.0591}{2}\log K_{sp}(\text{Hg}_2\text{Cl}_2)$

The standard potential of the calomel electrode is equal to 0.0455 + 0.222 = = 0.2675 V.

Thus, log $K_{sp}(\text{Hg}_2\text{Cl}_2)$ can be calculated as:

$$\log K_{sp}\,(\text{Hg}_2\text{Cl}_2) \;=\; \frac{2\left(0.2675 \;-\; 0.798\right)}{0.0591} = -17.99$$

$K_{sp} \;=\; 1.03\times10^{-18}$

PROBLEM 7

When the fresh-water rivers that run into the Chesapeake Bay flood after heavy rains in the spring, the increase in fresh water in the Bay causes a decrease in the salinity in the areas where oysters grow. The minimum concentration of chloride ions needed in oyster beds for normal growth is 8 ppm (8 mg dm^{-3}).

After one week of heavy rain, the following analysis is done on water from the bay. To a 50.00 cm^3 sample of bay water a few drops of a K_2CrO_4 solution are added. The sample is then titrated with 16.16 cm^3 of a 0.00164 M $AgNO_3$ solution. After $AgNO_3$ solution has been added to the sample a bright red-orange precipitate forms.

7.1 What is the molar concentration of chloride in the sample?

7.2 Does the water contain sufficient chloride for the normal growth of oysters? Show your calculation.

7.3 Write a balanced equation for the reaction of the analyte with the titrant.

7.4 Write a balanced net-ionic equation that describes the reaction responsible for the colour change at the endpoint of the titration. Which compound produces the brick-red colour?

7.5 The concentration of chromate at the endpoint is 0.020 M. Calculate the concentration of chloride ions in the solution when the red precipitate forms.

7.6 For this titration to work most effectively, the solution being titrated must be neutral or slightly basic. Write a balanced equation for the competing reaction that would occur in acidic medium that would influence the observed endpoint of this titration.

Typically, a buffer is added to the solution being titrated to control the pH if the initial sample is acidic. Suppose the *pH* of the sample of bay water was 5.10, thus too acidic to perform the analysis accurately.

7.7 Select a buffer from the list that would enable you to establish and maintain a *pH* of 7.20 in aqueous medium. Show the calculations which lead to your choice.

	Buffer systems	K_a of weak acid
1.	0.10 M lactic acid / 0.10 M sodium lactate	1.4×10^{-4}
2.	0.10 M acetic acid / 0.10 M sodium acetate	1.8×10^{-5}

3.	0.10 M sodium dihydrogen phosphate / / 0.10 M sodium hydrogen phosphate	6.2×10^{-8}
4.	0.10 M ammonium chloride / 0.10 M ammonia	5.6×10^{-10}

7.8 Using the selected buffer system, calculate the mass (in g) of weak acid and of conjugated base you would need to dissolve in distilled water to prepare 500 cm^3 of a stock solution buffered at a pH of 7.2.

7.9 The chloride concentration in another 50.00 cm^3 sample of bay water was determined by the Volhard method. In this method an excess of $AgNO_3$ is added to the sample. The excess Ag^+ is titrated with standardized KSCN, forming a precipitate of AgSCN. The endpoint is signalled by the formation of the reddish-brown $FeSCN^{2+}$ complex that forms when Ag^+ is depleted. If the excess Ag^+ from the addition of 50.00 cm^3 of 0.00129 M $AgNO_3$ to the water sample required 27.46 cm^3 of 1.41 10^{-3} M KSCN for titration, calculate the concentration of chloride in the bay water sample.

In natural waters with much higher concentration of Cl^-, the Cl^- can be determined gravimetrically by precipitating the Cl^- as AgCl. A complicating feature of this method is the fact that AgCl is susceptible to photodecomposition as shown by the reaction:

$$AgCl(s) \rightarrow Ag(s) + \frac{1}{2} Cl_2(g).$$

Furthermore, if this photodecomposition occurs in the presence of excess Ag^+, the following additional reaction occurs:

$$3\ Cl_2(g) + 3\ H_2O + 5\ Ag^+ \rightarrow 5\ AgCl + ClO_3^- + 6\ H^+$$

If 0.010 g of a 3.000 g sample of AgCl contaminated with excess Ag^+ undergoes photodecomposition by the above equations

7.10 Will the apparent weight of AgCl be too high or too low? Explain your answer showing by how many grams the two values will differ.

Data: $K_{sp}(AgCl) = 1.78 \times 10^{-10}$

$K_{sp}(Ag_2CrO_4) = 1.00 \times 10^{-12}$

SOLUTION

7.1 $n(\text{Ag}^+) = n(\text{Cl}^-)$

$$c(\text{Cl}^-) = \frac{0.01616\ \text{dm}^3 \times 0.00164\ \text{mol dm}^{-3}}{0.050\ \text{dm}^3} = 5.30\times10^{-4}\ \text{mol dm}^{-3}$$

7.2 Concentration in mg dm^{-3} = 5.30×10^{-4} mol dm^{-3} × 35.5 g mol^{-1} = 0.0188 g dm^{-3} = = 18.8 mg dm^{-3}

Thus the chloride concentration is sufficiently high for normal oyster growth.

7.3 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}\downarrow(\text{s})$

7.4 $2\ \text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4\downarrow(\text{s})$ (brick-red colour)

7.5 $K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 4\ x^3$ if $x = [\text{Ag}^+] \Rightarrow$

$[\text{Ag}^+] = 7.07 \times 10^{-6}$; $[\text{CrO}_4^{2-}] = 2 \times10^{-2}$

$$[\text{Cl}^-] = \frac{K_{sp}(\text{AgCl})}{\left[\text{Ag}^+\right]} = \frac{178 \times 10^{-10}}{7.07 \times 10^{-6}} = 2.5 \times 10^{-5}$$

7.6 $2\ \text{CrO}_4^{2-} + 2\ \text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$

either/or

$\text{CrO}_4^{2-} + \text{H}^+ \rightarrow \text{HCrO}_4^- + \text{H}_2\text{O}$

7.7 A buffer system has its maximum buffer capacity when $pH = pK_a$. So, the system 3 would be best since $pK_a = 7.2$

7.8 $m(\text{NaH}_2\text{PO}_4) = 0.10\ \text{mol dm}^{-3} \times 0.500\ \text{dm}^3 \times 119.98\ \text{g mol}^{-1} = 6.0\ \text{g}$

$m(\text{Na}_2\text{HPO}_4) = 0.10\ \text{mol dm}^{-3} \times 0.500\ \text{dm}^3 \times 141.96\ \text{g mol}^{-1} = 7.1\ \text{g}$

7.9 mol Ag$^+$ added: $n(\text{Ag}^+)_{\text{ad}} = 0.05\ \text{dm}^3 \times 0.00129\ \text{mol dm}^{-3} = 6.45\times10^{-5}$ mol

mol Ag$^+$ left over: $n(\text{Ag}^+)_{\text{left}} = 0.02746\ \text{dm}^3 \times 0.0141\ \text{mol dm}^{-3} = 3.87\times10^{-5}$ mol

mol Cl$^-$ in sample:

$n(\text{Cl}^-) = n(\text{Ag}^+)_{\text{ad}} - n(\text{Ag}^+)_{\text{left}} = (6.45\times10^{-5}\ \text{mol}) - (3.87\times10^{-5}\ \text{mol}) = 2.58\times10^{-5}$ mol

$$\Rightarrow \quad [\text{Cl}^-] = \frac{2.58\times10^{-5}}{0.050} = 5.16\times10^{-4}\ \text{mol dm}^{-3}$$

7.10 *n*(AgCl) lost: $\frac{0.010\text{ g AgCl}}{143.35\text{ gmol-1}} = 6.98 \times 10^{-5}$ mol

n(Cl_2) produced: ½ (6.98×10^{-5} mol) = 3.49×10^{-5} mol

n(AgCl) new prod.: 5/3 (3.49×10^{-5} mol) = 5.82×10^{-5} mol ≡ 8.34 mg

The amount of Ag formed is equal to the amount of AgCl lost, thus

$[Ag]_{formed} = 6.98\times10^{-5}\text{ mol} \times 107.9\text{ g mol}^{-1} = 7.53\times10^{-3}$ g

The mass of the sample is equal to 3.0 g – 0.010 g + 0.00834 g + 0.00753 g =

= 3.006 g. Therefore the total mass of the solid (AgCl + Ag) will be too high and the difference is 6 mg.

PROBLEM 2

The reflux of bile duodenal matter is suspected to be the major cause of gastritis and medical therapy is based on the treatment with antiacida that buffer the *pH* of gastric juices by binding bile acids and lysolecithin. Two bile acids, i. e. cholic acid (CA) and glycocholic acid (GCA), were chosen to study the properties of some antiacida commercial formulations. Separation and determination of the two acids in artificial and natural gastric juices were required and high performance liquid chromatography (HPLC) was used as analytical technique.

Two chromatographic columns (A and B, respectively) were selected on the base of published literature data and preliminary tests were carried out to choose the column (between A and B) which would yield the best separation of the aforementioned compounds. The retention times (*t*) of the two acids, of a substance not retained by the chromatographic columns and of a compound used as internal standard (i.s.) are shown in the first two columns of the Table. Both chromatographic columns are 25 cm long and show the efficiency of 2.56×10^4 theoretical plates per meter ($N\ m^{-1}$).

In actual analysis, an artificial gastric juice was extracted with an appropriate solvents mixture and then final solution (1 cm^3) contained 100 % of the two acids present in the original mixture. 100 μcm^3 of the extract with 2.7 μmoles of the internal standard were analysed by HPLC using the selected column. The response factors (F) of CA and GCA with respect to the i.s. and the chromatographic peak areas of the two compounds are reported in the Table.

	Column A *t* (s)	Column B *t* (s)	F	Area
Unretained compound	120	130	-	-
Cholic Acid (CA)	380	350	0.5	2200
Glycocholic Acid (GCA)	399	395	0.2	3520
Internal standard	442	430	-	2304

In answering to the questions remember that:

$$R = \frac{\sqrt{N}}{4} \times \frac{\alpha - 1}{\alpha} \frac{K'}{K'+1} \qquad (1)$$

$$\alpha = \frac{t_2'}{t_1'} = \frac{t_2 - t_0}{t_1 - t_0} \qquad (2)$$

$$K' = K_2' = \frac{t_2'}{t_0} = \frac{t_2 - t_0}{t_0} \qquad (3)$$

Questions:

2.1 Using *R*, α and *K'* values, demonstrate which of the two chromatographic columns would you use, considering that an accurate determination requires the best possible (baseline) separation of all compounds (do not take into account the unretained compound)?

2.2 Calculate the amounts of each acid in the extract solution.

SOLUTION

Nowadays, chromatography is the most powerful technique for the separation and quantification of organic compounds from volatiles to high molecular weight substances. In conjunction with a mass-spectrometer, it can lead to the undoubted identification of compounds even in extremely complex mixtures. Liquid chromatography (HPLC) is becoming a routine analytical technique in a large variety of fields and in particular in biochemistry and in medicine where compounds are unsuitable for gas chromatographic analysis.

2.1 Baseline separation requires R ≥ 1.5 for each pair of peaks (GCA/CA, i.s./GCA). N can be calculated from N m^{-1} value taking into account that the column length is 25 cm:

$N = 2.56\times10^4 \times (25/100) = 64\times10^2$

By substituting of α, *K* and *N* values in equation 1, the resolution for each pair of peaks can be found.

For column A:

$$\alpha_{GCA/CA} = \frac{399-120}{380-120} = \frac{279}{260} = 1.07$$

$$K'_{GCA} = \frac{399-120}{120} = 2.32$$

$$R_{GCA/CA} = \frac{\sqrt{64\cdot 10^2}}{4} \times \frac{0.07}{1.07} \times \frac{2.32}{3.32} = 0.91$$

$$\alpha_{i.s./GCA} = \frac{422-120}{399-120} = \frac{322}{279} = 1.15$$

$$K'_{i.s.} = \frac{442-120}{120} = 2.68$$

$$R_{i.s./GCA} = \frac{\sqrt{64\cdot 10^2}}{4} \times \frac{0.15}{1.15} \times \frac{2.68}{3.68} = 1.9$$

For column B:

$$\alpha_{GCA/CA} = \frac{395-130}{350-130} = \frac{265}{220} = 1.20$$

$$K'_{GCA} = \frac{395-130}{130} = 2.04$$

$$R_{GCA/CA} = \frac{\sqrt{64\cdot 10^2}}{4} \times \frac{0.20}{1.20} \times \frac{2.04}{3.04} = 2.2$$

$$\alpha_{i.s./GCA} = \frac{430-130}{395-130} = \frac{300}{265} = 1.13$$

$$K'_{i.s.} = \frac{430-130}{130} = 2.31$$

$$R_{i.s./GCA} = \frac{\sqrt{64\cdot 10^2}}{4} \times \frac{0.13}{1.13} \times \frac{2.31}{3.31} = 1.6$$

For column B the minimum value of R is 1.6 (>1.5) so that complete separation is obtained. For column A, R = 0.91 (<1.5) for the pair GCA/CA which, then, is not completely separated. Therefore column B should be used.

2.2 The amount of acid in the extract solution (1 cm^3) can be calculated from the relationship:

$$\frac{\mu\text{moles}_{\text{acid}}}{\mu\text{moles}_{\text{i.s.}}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F}$$

where F is the response factor.

Therefore:

$$\mu\text{moles}_{\text{acid}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F} \times \mu\text{moles}_{\text{i.s.}} \times \frac{1000}{100}$$

$$n(\text{CA}) = \frac{2200}{2304} \times \frac{1}{0.5} \times 2.7 \times 10 = 51.6\ \mu\text{mol}$$

$$n(\text{GCA}) = \frac{3520}{2304} \times \frac{1}{0.2} \times 2.7 \times 10 = 206\ \mu\text{mol}$$

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THEORETICAL PROBLEMS

PROBLEM 1

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. This will be illustrated by the following calculations:

Lactic acid written as HL is monoprotic, and the acid dissociation constant is $K_{HL} = 1.4\times10^{-4}$.

The acid dissociation constants for carbonic acid are: $K_{a1} = 4.5\times10^{-7}$ and $K_{a2} = 4.7\times10^{-11}$. All carbon dioxide remains dissolved during the reactions.

1.1 Calculate *pH* in a 3.00×10^{-3} M solution of HL.

1.2 Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate.

1.3 3.00×10^{-3} mol of lactic acid (HL) is added to 1.00 dm^3 of 0.024 M solution of $NaHCO_3$ (no change in volume, HL completely neutralized).

i) Calculate the value of *pH* in the solution of $NaHCO_3$ before HL is added.

ii) Calculate the value of *pH* in the solution after the addition of HL.

1.4 *pH* in the blood of a person changed from 7.40 to 7.00 due to lactic acid formed during physical activity. Let an aqueous solution having *pH* = 7.40 and $[HCO_3^-]$ = 0.022 represent blood in the following calculation. How many moles of lactic acid have been added to 1.00 dm^3 of this solution when its *pH* has become 7.00?

1.5 In a saturated aqueous solution of $CaCO_3(s)$ *pH* is measured to be 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant K_{sp} is 5×10^{-9}.

1.6 Blood contains calcium. Determine the maximum concentration of "free" calcium ions in the solution (*pH* = 7.40, $[HCO_3^-]$ = 0.022) given in 1.4.

SOLUTION

1.1 $HL + H_2O \rightarrow H_3O^+ + L^-$: $K_{HL} = 1.4\times10^{-4}$

$c_0 - x \qquad\qquad x \qquad x$

$$K_a = \frac{x^2}{c_0 - x} = 1.4\times10^{-4} \qquad\qquad c_0 = 3.00\times10^{-3}$$

Assumption $c_0 \gg x$ gives $x = 6.5 \cdot 10^{-4}$, not valid

Quadratic formula: $x = 5.8\times10^{-4}$, $[H_3O^+] = 5.8\times10^{-4}$, $pH = 3.24$

1.2 1: $HL + HCO_3^- \rightleftharpoons H_2CO_3 + L^-$: K_1

2: $HL + H_2O \rightleftharpoons H_3O^+ + L^-$: $K_2 = K_{HL}$

3: $HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$: $K_3 = \dfrac{1}{K_{a1}}$

Reaction 1 = 2 + 3, $K_1 = K_2 \cdot K_3 = 311$ (3.1×10^2)

Alternative: $K_1 = \dfrac{[H_2CO_3]\,[L^-]}{[HL]\,[HCO_3^-]} \times \dfrac{[H_3O^+]}{[H_3O^+]} = \dfrac{[H_3O^+][L^-]}{[HL]} \times \dfrac{[H_2CO_3]}{[HCO_3^-][H_3O^+]}$

1.3 i) HCO_3^- is amphoteric, $pH \approx \dfrac{1}{2}(pK_{a1} + pK_{a2}) = \underline{8.34}$

ii) $HL + HCO_3^- \rightleftharpoons H_2CO_3 + L^-$, "reaction goes to completion"

Before: 0.0030 0.024 0 0

After : 0 0.021 0.0030 0.0030

Buffer: $pH \approx pK_{a1} + \log\dfrac{0.021}{0.0030} = 6.35 + 0.85 = 7.20$

(Control: $\dfrac{K_{HL}}{[H_3O^+]} = \dfrac{[L^-]}{[HL]} = 2.2\times10^3$, assumption is valid)

1.4 A: $pH = 7.40$; $[H_3O^+] = 4.0\times10^{-8}$; $[HCO_3^-]_A = 0.022$.

From K_{a1}: $[H_2CO_3]_A = 0.0019$;

(1) $[HCO_3^-]_B + [H_2CO_3]_B = 0.0239$ (0.024)

B: $pH = 7.00$; $\dfrac{[HCO_3^-]}{[H_2CO_3]} = 4.5$;

(2) $[HCO_3^-]_B = 4.5\,[H_2CO_3]_B$

From (1) and (2): $[HCO_3^-]_B = 0.0196$

$[H_2CO_3]_B = 0.0043$

$n(HL) = \Delta n(H_2CO_3) = \Delta c(H_2CO_3) \times 1.00\ dm^3 = 2.4\times10^{-3}$ mol

1.5 $[OH^-] = 8.9\times10^{-5}$ $[H_2CO_3]$ of no importance

Reactions: A: $CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$

c_0 c_0

B: $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ $K = K_b = 2.1\times10^{-4}$

$c_0 - x$ x x

From B: $[HCO_3^-] = [OH^-] = 8.9\times10^{-5}$

$$[CO_3^{2-}] = \frac{[HCO_3^-][OH^-]}{K_b} = 3.8\times10^{-5}$$

$[Ca^{2+}] = [HCO_3^-] + [CO_3^{2-}] = 1.3\times10^{-4}$

$c_0(Ca^{2+}) = 1.3\times10^{-4}\ mol\ dm^{-3}$ = solubility

1.6 $K_{sp} = [Ca^{2+}]\,[CO_3^{2-}] = 1.3\times10^{-4} \times 3.8\times10^{-5} = 4.9\times10^{-9} = \mathbf{5\times10^{-9}}$

From K_{a2} : $$[CO_3^{2-}] = \frac{K_{a_2}\,[HCO_3^-]}{[H_3O^+]} = 2.6\times10^{-5}$$

$Q = [Ca^{2+}]\,[CO_3^{2-}]$; Precipitation when $Q > K_{sp} = 5\times10^{-9}$

No precipitation when $Q < K_{sp}$

Max. concentration of "free" Ca^{2+} ions:

$$[Ca^{2+}]_{max} = \frac{K_{sp}}{[CO_3^{2-}]} = 1.9\times10^{-4}$$

PROBLEM 2

Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

2.1 0.2515 g of a grain sample was treated with sulphuric acid, sodium hydroxide was then added and the ammonia distilled into 50.00 cm^3 of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 cm^3 of 0.1050 M sodium hydroxide.

Calculate the concentration of nitrogen in the sample, in percent by mass.

2.2 Calculate the *pH* of the solution which is titrated in 2.1 when 0 cm^3, 9.65 cm^3, 19.30 cm^3 and 28.95 cm^3 of sodium hydroxide have been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid. K_a for ammonium ion is 5.7×10^{-10}.

2.3 Draw the titration curve based on the calculations in b).

2.4 What is the *pH* transition range of the indicator which could be used for the back titration.

2.5 The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occurring amino acid was determined by digesting 0.2345 g of the pure acid and distilling ammonia released into 50.00 cm^3 of 0.1010 M hydrochloric acid. A titration volume of 17.50 cm^3 was obtained for the back titration with 0.1050 M sodium hydroxide.

Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

SOLUTION

2.1 $$[(50.00 \times 0.1010) - (19.30 \times 0.1050)]\,\frac{14.01}{1000} \times \frac{100}{0.2515} = 16.84\ \%\ \text{N}$$

2.2 0 cm^3 added: $$[\text{H}^+] = \frac{19.30 \cdot 0.1050}{50} = 0.04053$$

$$pH = 1.39$$

9.65 cm^3 added: $[H^+] = \quad = 0.01699$

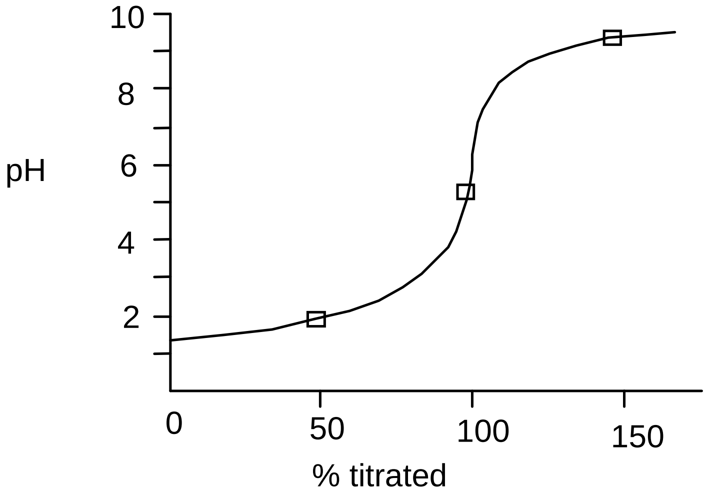
$pH = 1.77$

19.30 cm^3 added: $$[H^+] = \sqrt{5.7 \cdot 10^{-10} \times \frac{50.00 \cdot 0 \times 101019 \times 30 \cdot 0 \times 1050}{50 + 19.30}}$$

$pH = 5.30$

28.95 cm^3 added: $$\boldsymbol{pH} = pK_a + \log \frac{[NH_3]}{[NH_4^+]} = 9.24 + \log \frac{1.01}{2.01} = 8.94$$

2.3



2.4 Indicator *pH* transition range: *pH* 5.3 ± 1

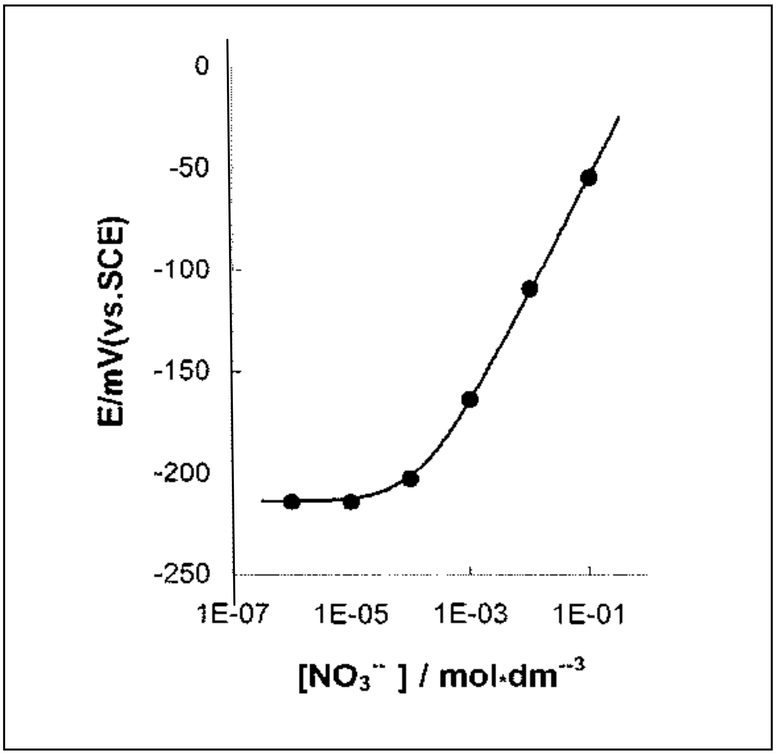
2.5 $$[(50.00 \times 0.1010) - (17.50 \times 0.1050)] \frac{14.01}{1000} \times \frac{100}{0.2345} = 19.19 \text{ \% N}$$

1 N: $M_r = 73.01$ 2 N: $M_r = 146.02$

PROBLEM 2

To control the quality of milk serum, a dairy by-product, the concentration of NO_3^- ion in serum is monitored by means of an ion selective electrode. Generally there is about 15 mg NO_3^- ion per litre in serum, measured on the basis of nitrogen mass.

2.1 For a nitrate ion selective electrode a calibration curve as shown below was obtained using a series of standard nitrate solutions containing 0.5 mol dm^{-3} K_2SO_4, 1.0×10^{-3} mol dm^{-3} H_2SO_4 and 2.6×10^{-3} mol dm^{-3} Cl^- ion as the background. Decide whether it is feasible to measure concentration NO_3^- in serum under the above conditions.



2.2 Given are selective coefficients of Cl^-, SO_4^{2-} and ClO_4^- versus NO_3^- as follow

$$K_{NO_3^-,Cl^-} = \frac{c_{NO_3^-}}{c_{Cl^-}} = 4.9\times10^{-2} \quad K_{NO_3^-,SO_4^{2-}} = \frac{c_{NO_3^-}}{c_{SO_4^{2-}}^{1/2}} = 4.1\times10^{-3}$$

$$K_{NO_3^-,ClO_4^-} = \frac{c_{NO_3^-}}{c_{ClO_4^-}} = 1.0\times10^{-3}$$

where the units of the concentrations are in mol dm^{-3} which is the best to reduce the interference of Cl^- to NO_3^- determination, so as to control the error in the NO_3^- concentration within 1 %, when there are 1.40×10^{-3} mol dm^{-3} NO_3^- and 1.60×10^{-2} mol dm^{-3} Cl^- in serum:

(a) $AgNO_3$ (b) Ag_2SO_4 (c) $AgClO_4$

Calculate the amount of the salt that should be added to 1 dm^3 of the sample solution to be measured.

2.3 The NO_3^- ion concentration was determined by this method at 298 K. For 25.00 cm^3 sample solution the electronic potential, *E*, is measured to be –160 mV. After adding 1.00 cm^3 1.00×10^{-3} mol dm^{-3} NO_3^- standard solution to the above solution, ***E*** changes to –130 mV. Find the pNO_3 of the serum.

2.4 The selective coefficient of CH_3COO^- versus NO_3^- $K(NO_3^-/CH_3COO^-) = 2.7\times10^{-3}$. If $AgCH_3COO$ instead of Ag_2SO_4 is added to the sample solution of question 2.2, find the upper limit of the *pH* value below which the same requirement in question 2.2 can be met.

$K_{sp}(AgCl) = 3.2\times10^{-10} K_{sp}(Ag_2SO_4) = 8.0\times10^{-5}$

$K_{sp}(AgCH_3COO) = 8.0\times10^{-3}$ $K_a(CH_3COOH) = 2.2\times10^{-5}$

$A_r(N) = 14.00$

SOLUTION

2.1 Yes

2.2 B

$(1.4\times10^{-3} \times 0.01) / [Cl^-] = 4.9\times10^{-4}$ mol dm^{-3}

$[Cl^-] = 2.9\times10^{-4}$ mol dm^{-3}

Excess $[Cl^-] = 1.6\times10^{-2} - 2.9\times10^{-3} \cong 1.6\times10^{-2}$ mol dm^{-3}

To reduce the interference of Cl^- at least 1.6×10^{-2} mol Ag^+ ion or 8.0×10^{-3} mol Ag_2SO_4 has to be added to 1 dm^3 sample solution.

2.3 $\Delta E = E_2 - E_1 = 0.059 \log \{(c_X V_X + c_S V_S)(c_X [V_x + V_S])\}$

$0.03 = 0.059 \log [(25.00\ V_x + 0.10) / (26.00 \times c_x)]$

$c_x = 1.7\times10^{-3}$ mol dm^{-3}

$p\mathrm{NO_3} = 2.77$

2.4 $pH = 4.4$

$(1.4\times10^{-3} \times x) \div 1.6\times10^{-2} = 2.7\times10^{-3}$

$x = 3.1\ \% > 1\ \%$

$(1.4\times10^{-3} \times 0.01) \div [\mathrm{CH_3COO^-}] = 2.7\times10^{-3}$

$[\mathrm{CH_3COO^-}] = 5.2\times10^{-3}$ mol dm^{-3}

$1.6\times10^{-2} - 5.2\times10^{-3} = 1.08\times10^{-2}$ mol dm^{-3}

$\{[\mathrm{H^+}] \times 5.2\times10^{-3}\} \div (1.08\times10^{-2}) = 2.2\times10^{-5}$

$[\mathrm{H^+}] = 4.3\times10^{-5}$ mol dm^{-3}

$pH = 4.4$

PROBLEM 6

A surfactant molecule can generally be modelled as Fig. 1 where a circle presents the polar head (PH), i.e. the hydrophilic part of the molecule, and a rectangle represents the non-polar tail (NT), i. e. the hydrophobic part of the molecule.

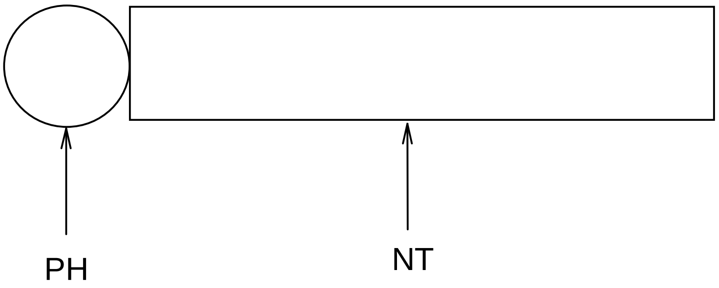


Fig. 1

6.1 AOT is a surfactant. Its systematic name (IUPAC name) is sulfobutanedioic acid 1,4-bis-(2-ethylhexyl) ester sodium salt (formula $C_{20}H_{37}NaO_7S$).

i) Write the structural formula for AOT and fill its PH and NT in the circle and rectangle on your answer sheet.

ii) Choose the type of surfactant AOT among the following.

a) Non-ionic; b) Anionic; c) Cationic; d) Others.

6.2 Mixing an aqueous solution of 50 mmol AOT with isooctane (volume ratio 1 : 1), a micellar extraction system will be formed in the isooctane phase (organic phase).

i) Using the model as shown in Fig. 1, draw a micelle with 10 AOT molecules under the given condition.

ii) What species are in the inner cavity of this micelle? Write their chemical formulas.

6.3 There is an aqueous solution containing the proteins as listed below:

Protein	Molecular mass (M_r)×10^4	Isoelectronic point (PI)
A	1.45	11.1
B	1.37	7.8
C	6.45	4.9
D	6.80	4.9
E	2.40	4.7
F	2.38	0.5

The separation of proteins can be performed by mixing the AOT micellar extraction system with the solution. Adjusting the *pH* value of the solution to 4.5, only three of the above listed six proteins can be extracted into the micelles. Which proteins will be extracted?

6.4 The three proteins entered into the micelles will be separated from each other by the following procedure shown as in Fig. 2. Each extracted protein can be sequentially transported into a respective water phase.

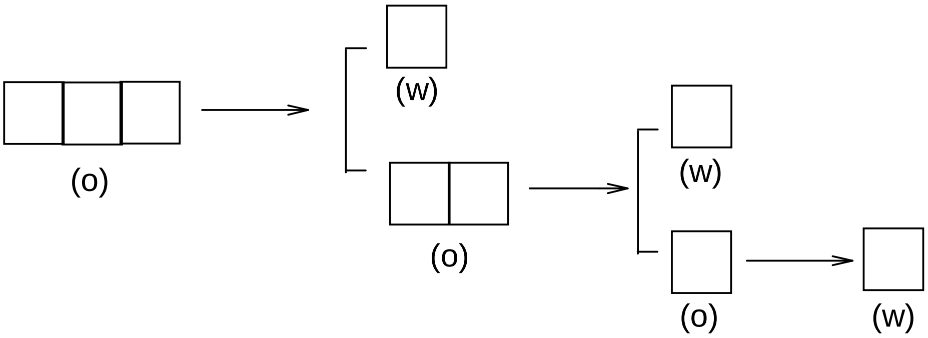


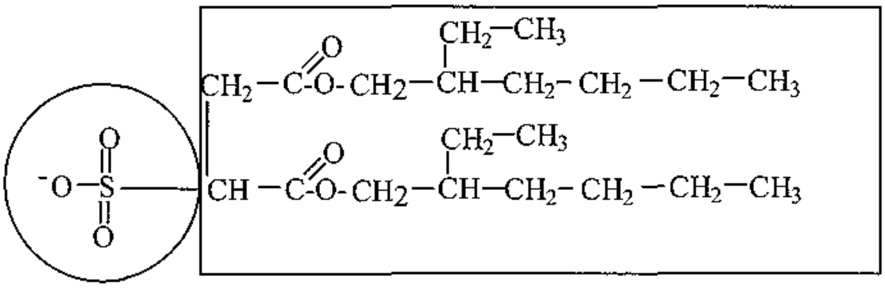
Fig. 2

Note: (w) represents water phase; (o) represents organic phase

Fill the three extracted proteins in the left boxes first and then separate them by the procedure given, and give the separation conditions above each arrow as well.

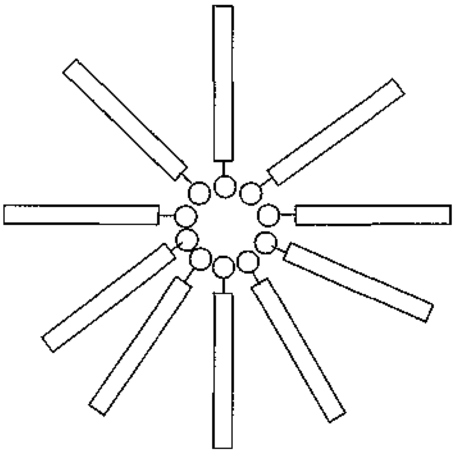
SOLUTION

6.1 i)



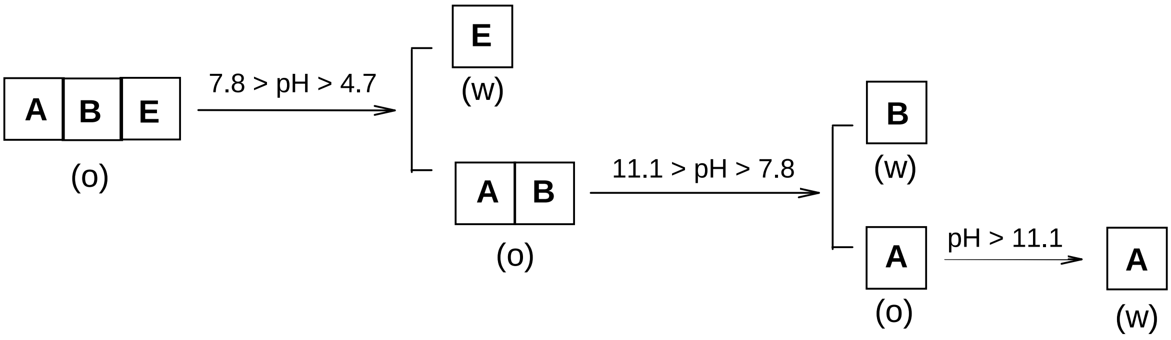
ii) (b)

6.2 i)



6.3 **A**, **B**, and **E**.

6.4



PROBLEM 2

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy.

As an example we shall consider the method used for the determination of microscopic amounts of bismuth. In 1927 German chemist Berg suggested to precipitate bismuth as a practically insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate $[C_9H_6(OH)NH][BiI_4]$ ($M_r = 862.7$).

2.1 a) Draw the structural formulae of the cation and anion of this salt.

b) What is the oxidation state of Bi atom in this compound?

2.2 Evaluate the smallest mass of bismuth (in *mg*), which can be determined reliably by Berg method, if the smallest mass of precipitate which can be reliably measured is 50.0 mg.

For the determination of trace amounts of bismuth R. Belcher and co-workers from Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

Step 1: To a given small amount (≈ 2 cm^3) of cold acidified solution containing trace amounts of Bi^{3+} 50 mg of potassium hexathiocyanatochromate(III) ($K_3[Cr(SCN)_6]$) is added in the cold, that leads to practically quantitative precipitation of bismuth.

2.3 Write a balanced net ionic equation of this reaction.

Step 2: The precipitate is filtered off, washed by cold water, and treated with 5 cm^3 of 10 % solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate transforms into the precipitate of oxobismuth(III) carbonate $(BiO)_2CO_3$ with liberation of hexathiocyanatochromate(III) ions into solution.

2.4 Write a balanced net ionic equation of this reaction.

Step 3: To the slightly acidified filtrate transferred to a separatory funnel 0.5 cm^3 of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidizes the ligand of the complex ion to ICN and sulphate ion.

2.5 Write a balanced net ionic equation of this reaction.

Step 4: Upon 5 minutes 4 cm^3 of 2 M H_2SO_4 solution are added to the mixture. The acidification leads to the reaction of coproportionation with the evolution of molecular iodine.

2.6 Write a balanced net ionic equation of the reaction occurred on acidification.

Step 5: Iodine is quantitatively extracted by 4 portions of chloroform. Aqueous layer is transferred to a flask, to which 1 cm^3 of bromine water is added, and the mixture is mixed for 5 minutes.

2.7 Write the balanced net ionic equations of the reactions occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give BrCN, and iodide is oxidized into IO_3^-.

Step 6: To eliminate an excess of molecular bromine 3 cm^3 of 90 % methanoic (formic) acid is added to the mixture.

2.8 Write a balanced net ionic equation of this reaction.

Step 7: To the slightly acidic solution an excess (1.5 g) of potassium iodide is added.

2.9 Write the balanced net ionic equations of the reactions occurred upon the addition of KI, taking into consideration that iodide reacts with BrCN in a similar manner as with ICN to form molecular iodine.

Step 8: The resulting solution is titrated by a standard 0.00200 M $Na_2S_2O_3$ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

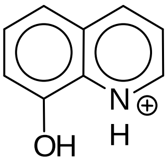
2.10 a) How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

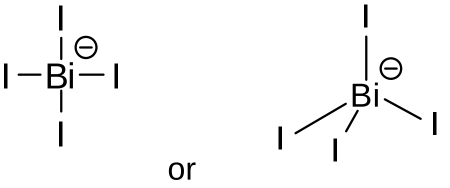
b) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm^3 of standard 0.00200 M $Na_2S_2O_3$ solution)?

2.11 By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

SOLUTION

2.1 a)





Cation Anion

b)

The oxidation number of bismuth in 8-hydroxyquinolinium tetraiodobismuthate: **III**

2.2 The smallest mass of bismuth determined reliably by Berg method, 12.1 mg.

Molar mass of the precipitate is 862.7 g, which contains 209.0 g of bismuth. Thus, 0.0500 g of the precipitate correspond to 1.21×10^{-2} g = 12.1 mg of bismuth.

2.3 $Bi^{3+} + [Cr(SCN)_6]^{3-} \longrightarrow Bi[Cr(SCN)_6]$.

2.4 $2\ Bi[Cr(SCN)_6] + 6\ HCO_3^- \longrightarrow (BiO)_2CO_3 + 2\ [Cr(SCN)_6]^{3-} + 3\ H_2O + 5\ CO_2$

or

$2Bi[Cr(SCN)_6] + HCO_3^- + 5\ OH^- \longrightarrow (BiO)_2CO_3 + 2\ [Cr(SCN)_6]^{3-} + 3\ H_2O$ etc.

(variations are possible)

2.5 $[Cr(SCN)_6]^{3-} + 24\ I_2 + 24\ H_2O \longrightarrow Cr^{3+} + 6\ SO_4^{2-} + 6\ ICN + 42\ I^- + 48\ H^+$

2.6 $ICN + I^- + H^+ \longrightarrow I_2 + HCN$

2.7 a)

$3\ Br_2 + I^- + 3\ H_2O \longrightarrow IO_3^- + 6\ Br^- + 6\ H^+$

b)

$Br_2 + HCN \longrightarrow BrCN + Br^- + H^+$

Comment: From reaction 2.5 it is evident that considerably more of ions I^- are formed than of ICN molecules. Therefore, after the completion of reaction 2. 6 an excess of I^- ions will be left.

2.8 $Br_2 + HCOOH \longrightarrow 2\ Br^- + CO_2 + 2\ H^+$

2.9 a)

$IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$

b)

$BrCN + 2I^- + H^+ \longrightarrow I_2 + HCN + Br^-$

2.10 a)

228 moles of thiosulphate correspond to 1 mole of bismuth.

b)

The least mass of bismuth, $1.83 \cdot 10^{-3}$ mg

Solution:

a)

Titration of iodine by thiosulphate involves the reaction:

$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$.

Assume that the initial solution contained 1 mole of Bi. In the reaction 5 each mole of Bi leads to the formation of 42 moles of iodide (for convenience divide all coefficients of reaction 4 by 2), of which 6 moles of iodide-ion was consumed in reaction 2.6. Thus, 36 moles of iodide was consumed in reaction 2.7a) to give 36 moles of IO_3^-, which in reaction 2.9a) gave 36 × 3 = 108 moles of I_2, which take 108 × 2 = 216 moles of thiosulphate for titration. However, that is not all. Indeed, 6 moles of HCN are generated per mole of Bi^{3+} according to reactions 2.5 and 2.6. The oxidation of HCN by bromine in reaction 2.7b) gives 6 moles of BrCN, which in its turn in reaction 2.9b) gives 6 moles of iodine taking 12 more moles of thiosulphate. Thus, total amount of thiosulphate is 216 + 12 = 228.

b)

1.00 cm^3 of 0.00200 M thiosulphate solution contains 2.00×10^{-6} mole of $Na_2S_2O_3$, which corresponds to $209.0 \times 2.00 \times 10^{-6} / 228 = 1.83 \times 10^{-6}$ g $= 1.83 \times 10^{-3}$ mg = = 1.83 μg**.**

2.11 $$\frac{\text{Detection limit of gravimetric method}}{\text{Detection limit of multiplicated method}} = 6600$$

The multiplicative method is more sensitive than the gravimetric method by 12.1 mg / 1.83×10^{-3} mg = 6600 times.

PROBLEM 4

The precipitation is widely used in classical methods of the quantitative and qualitative analysis for the separation of ions. The possibility of separation is determined by the equilibrium concentrations of all species in a solution to be analyzed.

Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).

$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-}$ log K_1 = -6.50

$2\,HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$ log K_2 = 1.36

4.1 Calculate the equilibrium constants

a) $CrO_4^{2-} + H_2O \rightleftarrows HCrO_4^- + OH^-$

b) $Cr_2O_7^{2-} + 2\,OH^- \rightleftarrows 2\,CrO_4^{2-} + H_2O$

The ionic product of water $K_W = 1.0\times10^{-14}$.

4.2 In what direction shall the equilibrium state 1b shift upon the addition of the following reagents to the aqueous solution of potassium dichromate?

a) KOH

b) HCl

c) $BaCl_2$

d) H_2O

The solubility product of $BaCrO_4$ is 1.2×10^{-10}. $BaCr_2O_7$ is well soluble in water.

4.3 Calculate the pH value of the following solutions

a) 0.010 M K_2CrO_4

b) 0.010 M $K_2Cr_2O_7$

c) 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COOH

Dissociation constant of acetic acid $K_a = 1.8\times10^{-5}$.

4.4 Calculate the equilibrium concentrations of the following ions in the solution of 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COOH

a) CrO_4^{2-}

b) $Cr_2O_7^{2-}$

Pb^{2+} and Ag^+ form poorly soluble compounds with chromate and dichromate ions. The solubility products of these compounds are indicated below.

$PbCrO_4$ $K_{s1} = 1.2\times10^{-14}$

Ag_2CrO_4 $K_{s2} = 1.3\times10^{-12}$

$Ag_2Cr_2O_7$ $K_{s3} = 1.1\times10^{-10}$

To the aqueous solution of the mixture of 1.0×10^{-3} M $Pb(NO_3)_2$ and 2.0×10^{-4} M $AgNO_3$ an equal volume of 0.020 M solution of $K_2Cr_2O_7$ in 0.200 M CH_3COOH was added.

4.5 a) Shall Pb^{2+} be precipitated?

b) Shall Ag^+ be precipitated?

c) Shall a quantitative separation of Pb^{2+} and Ag^+ ions be thus achieved?

The quantitative precipitation is achieved if the residual concentration of the ion being precipitated is not higher than 1×10^{-6} M.

SOLUTION

4.1

a)

Equilibrium constant = 3.2×10^{-8}

$$\frac{[HCrO_4^-]\,[OH^-]}{[CrO_4^{2-}]} = \frac{[HCrO_4^-]\,[OH^-]\,[H^+]}{[CrO_4^{2-}]\,[H^+]} = \frac{K_w}{K_1}$$

$$\frac{1.0\times10^{-14}}{3.16\times10^{-7}} = 3.2\times10^{-8}$$

b) Equilibrium constant > 4.4×10^{13}

$$\frac{K_1^2}{K_2\,K_w^2} = \frac{\left(\dfrac{\left[CrO_4^{\ 2-}\right]\left[H^+\right]}{\left[HCrO_4^{\ -}\right]}\right)^2}{\dfrac{\dfrac{\left[HCrO_4^{\ -}\right]^2}{\left[Cr_2O_7^{\ 2-}\right]}}{\left(\left[H^+\right]\left[OH^-\right]\right)^2}} = \frac{10^{-2\times6.50}}{10^{1.36}\times10^{-2\times14.00}} = 10^{13.64} = 4.4\times10^{13}$$

4.2 Place a checkmark at the correct answer

The equilibrium will	shift to left	shift to right	not shift
a)		☑	
b)	☑		
c)		☑	
d)		☑	

Calculations:

In case a) and b) the answer is self-evident.

c) $BaCl_2$ shifts the equilibrium to the right due to the binding of chromate ion into a poorly soluble compound

$Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4$

d) This answer may appear as strange, as water is among the products specified in the right part of the equilibrium equation. However, this is too formal. Actually in dilute aqueous solutions the concentration of water may be regarded as fairly constant and the addition of water would not affect it. Nevertheless, the addition of water to dichromate solution leads to the dilution, which in its turn shifts the dichromate ion dissociation equilibrium to the right. Second, in the aqueous solution of $K_2Cr_2O_7$ the value of pH < 7 due to the processes described in the problem statement (cf. also the solution to 3b). With the dilution of any aqueous solution pH is varying towards 7, that in this case means the increase of pH. This also shifts the equilibrium to the right.

4.3 a) $pH = 9.25$

b) $pH = 4.20$

c) $pH = 2.87$

Calculations:

a) $CrO_4^{2-} + H_2O = HCrO_4^{-} + OH^{-}$ $K = 3.16\times10^{-8}$

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^{-}] + 2\,[Cr_2O_7^{2-}] \approx [CrO_4^{2-}]$,

$[HCrO_4^{-}] \approx [OH^{-}]$

$[OH^-]^2/c_{Cr} = K$, $[OH^-] = \sqrt{K\ c_{Cr}} = \sqrt{3.16\times10^{-8}\times0.01} = 1.78\times10^{-5}$

$[H^+] = 5.65\cdot10^{-10}$, $pH = 9.25$

b) $Cr_2O_7^{2-} + H_2O = 2\ HCrO_4^-$ $K = 1/K_2 = 4.37\times10^{-2}$

$HCrO_4^- = H^+ + CrO_4^{2-}$ $K = K_1 = 3.16\times10^{-7}$

$[H^+] \approx [CrO_4^{2-}] \Rightarrow [H^+] = \sqrt{K_1[HCrO_4^{2-}]}$

$[HCrO_4^-]$ = ?

$c_{Cr} = 2.0\cdot10^{-2}$ M (**) $= [CrO_4^{2-}] + [HCrO_4^-] + 2\ [Cr_2O_7^{2-}] \approx [HCrO_4^-] + 2\ [Cr_2O_7^{2-}]$

$[HCrO_4^-] = x$; $K_2 = [Cr_2O_7^{2-}]/\ [HCrO_4^-]^2 = (c_{Cr} - x)\ /\ 2x^2$; $2\ K_2x^2 + x - c_{Cr} = 0$

hence $[H^+] = (3.16\times10^{-7}\times1.27\times10^{-2})^{1/2} = 6.33\times10^{-5}$; pH = 4.20

c) In 0.10 M CH_3COOH $[H^+] = (K_a\ c)^{1/2/}$ (*) $= (1.8\times10^{-5}\times0.10)^{1/2} = 1.34\times10^{-3}$

$pH = 2.87$

4.4 Equilibrium concentrations

a)	3.0×10^{-6}
b)	3.7×10^{-3}

Calculations:

The different methods can be used.

Method 1.

a)

$[HCrO_4^-] = 1.3\times10^{-2}$ (*)

$[CrO_4^{2-}] = K_1[HCrO_4^-]\ /\ [H^+] = 3.16\times10^{-7}\times1.3\times10^{-2}\ /\ 1.34\times10^{-3} = 3.0\times10^{-6}$

b)

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2\ [Cr_2O_7^{2-}]$

$[Cr_2O_7^{2-}] = ½(c_{Cr} - [CrO_4^{2-}] - [HCrO_4^-]) = ½\ (2.0\times10^{-2} - 3.0\times10^{-6} - 1.3\times10^{-2}) = 3.7\times10^{-3}$

or otherwise

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-]^2 = 22.9\times(1.3\times10^{-2})^2 = 3.9\times10^{-3}$

Method 2

a)

$[CrO_4^{2-}] = x$; $[HCrO_4^-] = x[H^+] / K_1$

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = x^2 K_2 [H^+]^2 / K_1^2$

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] = 2K_2 [H^+]^2 / K_1^2 x^2 + (1 + [H^+] / K_1)x$

$K_1 = 3.16\times10^{-7}$; $K_2 = 22.9$; $[H^+] = 1.34\times10^{-3}$

$8.24\times10^8 x^2 + 4.24\times10^3 x - 2.0\times10^{-2} = 0$

$x = 3.0\times10^{-6}$

b)

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = K_2 [H^+]^2 / K_1^2 [CrO_4^{2-}]^2 = 4.12\times10^8 \times (3.0\times10^{-6})^2 = 3.7\times10^{-3}$

PROBLEM 5

Potentiometric and spectrophotometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution. Both methods are frequently used in combination to achieve simultaneous determination of several species.

Solution **I** contains a mixture of $FeCl_2$ (aq)) and $FeCl_3$(aq), and solution **II** contains a mixture of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. The concentrations of iron-containing species satisfy the relations $[Fe^{2+}]_I = [Fe(CN)_6^{4-}]_{II}$ and $[Fe^{3+}]_I = [Fe(CN)_6^{3-}]_{II}$. The potential of platinum electrode immersed into the solution **I** is 0.652 V, while the potential of platinum electrode immersed into solution II is 0.242 V. The transmittance of the solution **II** measured relative to the solution **I** at 420 nm is 10.7 % (optical pathlength *l* = 5.02 mm). The complexes $Fe(CN)_6^{4-}$, $Fe(H_2O)_6^{3+}$, and $Fe(H_2O)_6^{2+}$ do not absorb light at 420 nm.

Molar absorption at this wavelength $\varepsilon([Fe(CN)_6^{3-}]) = 1100\ M^{-1}\ cm^{-1}$.

Standard redox potential for $Fe(H_2O)_6^{3+}$ / $Fe(H_2O)_6^{2+}$ is 0.771 *V*.

The factor before the logarithm in the Nernst equation is 0.0590.

5.1 Write Nernst equations for redox systems of

a) solution **I**,

b) solution **II**.

5.2 What are the units of the pre-logarithm factor 0.0590 in the Nernst equation?

5.3 Calculate the ratio of the stability constants $\beta[Fe(CN)_6^{3-}]$ / $\beta[Fe(CN)_6^{4-}]$.

5.4 What is the absolute range of variation for the following physical values

a) transmittance *T*;

b) absorbance *A*.

5.5 Sketch the graphs of concentration dependences satisfying the Lambert-Beer law for

a) absorbance *A*;

b) transmittance *T*;

c) molar absorption ε.

5.6 Calculate the concentrations of

a) Fe^{2+} in solution **I**;

b) Fe^{3+} in solution **II**.

5.7 Mixing solutions **I** and **II** gives intense blue colour. What species is characterized by this colour? Write the reaction equation.

SOLUTION

5.1 Nernst equations:

a) $E_I = E°(Fe^{3+}/Fe^{2+}) + 0.0590 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$

b) $E_I = E°(Fe(CN)_6^{3-}/ Fe(CN)_6^{4-}) + 0.0590 \log \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]}$

5.2 The units of pre-logarithm factor: V

5.3 The ratio of stability constants

$\beta\{Fe(CN)_6^{3-}\} / \beta\{Fe(CN)_6^{4-}\} = 8.90\times10^6$

Calculations:

$$E_{II} = E°(Fe(CN)_6^{3-}/Fe(CN)_6^{4-}) + 0.0590 \log[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] =$$

$$= E°(Fe^{3+}/Fe^{2+}) + 0.0590 \log(\beta_1/\beta_2) + 0.0590 \log([CN^-]^6/[CN^-]^6) +$$

$$+ 0.0590 \log[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] = 0.242$$

(where β_1 and β_2 are stability constants for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively.)

$[Fe(CN)_6^{3-}] / [Fe(CN)_6^{4-}] = [Fe^{3+}] / [Fe^{2+}]$, therefore

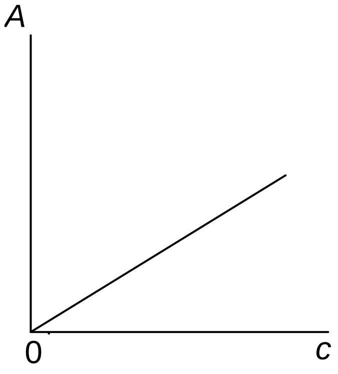
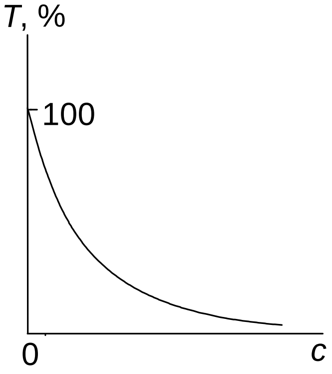
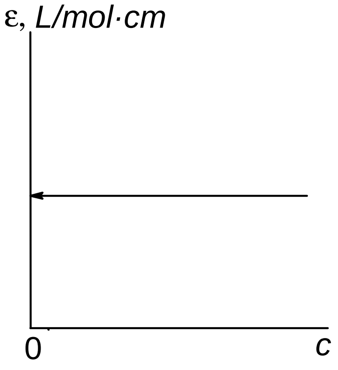
$\Delta E = E_{II} - E_I = 0.0590\cdot\log(\beta_1/\beta_2)$, and $\beta_2/\beta_1 = 8.90\times10^6$.

5.4 The ranges of variation:

a) from 0 to 100

b) from 0 to ∞

5.5

a)	b)	c)
		

5.6 a) Using Bouger-Lambert-Beer law

$$A = \varepsilon l c = \varepsilon l c[\text{Fe(CN)}_6^{3-}] = 0.971;$$

$$c[\text{Fe(CN)}_6^{3-}] = 0.971/(1100 \times 0.502) = 1.76\times10^{-3}\ \text{M} = c[\text{Fe}^{3+}]$$

b) using Nernst's equation

$E = E°(\text{Fe}^{3+} / \text{Fe}^{2+}) + 0.0590 \log[\text{Fe}^{3+}]_I / [\text{Fe}^{2+}]_I =$

$= 0.771 + 0.0590 \log [\text{Fe}^{3+}]_I / [\text{Fe}^{2+}]_I = 0.652\ V.$

hence,

$[\text{Fe}^{3+}]_I / [\text{Fe}^{2+}]_I = 9.62\times10^{-3};$

$[\text{Fe}^{2+}]_I = 1.76\times10^{-3} / 9.62\times10^{-3} = 0.183$ M.

PROBLEM 4

Graph paper is provided for your optional use in this question.
If you choose to use it, print your name and identification code in the upper right corner of the graph paper.

****

HIn is a weakly acidic indicator.

$HIn + Na+OH- \rightleftarrows Na+In- + H_2O$

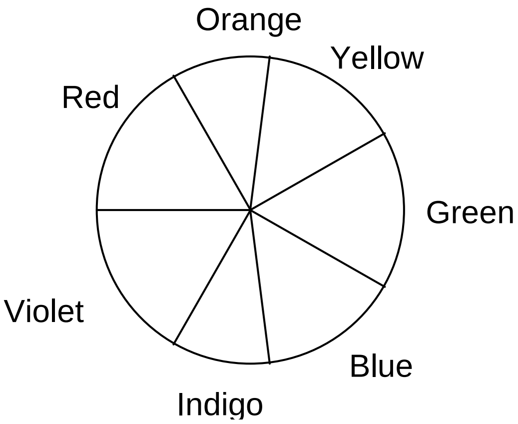
also written as

$HIn \rightleftarrows In- + H^+$

At normal temperatures, the acid dissociation constant for this indicator is $K_a = 2.93 \times 10^{-5}$. The absorbance data (1.00 cm cells) for 5.00×10^{-4} M (mol dm^{-3}) solutions of this indicator in strongly acidic and strongly alkaline solutions are given in the following table.

Absorbance Data (A)

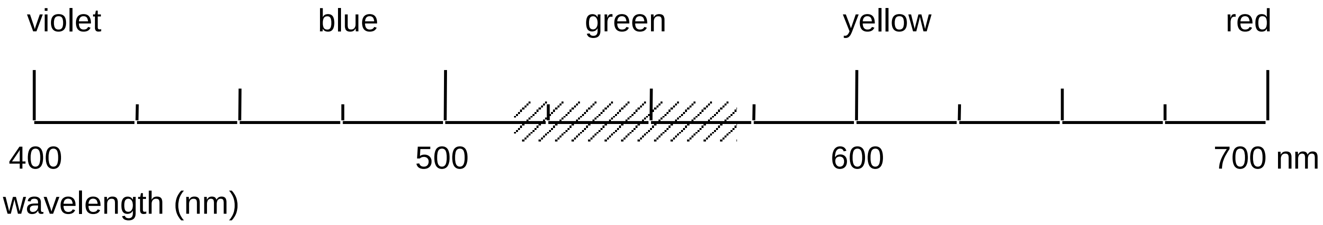
λ, nm	*pH* = 1.00	*pH* = 13.00
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588



4.1 Predict the observed colour of the a) acidic and b) basic forms of the indicator.

Using a "50 nm wide bar", shade the appropriate area of the wavelength scale on the answer sheet which would correspond to the colour of the indicator at the *pH* values given in the table.

For example, if observed colour is green, your answer would appear as:



4.2 A filter is located between the light source and the sample. What colour filter would be most suitable for the photometric analysis of the indicator in a strongly acidic medium?

4.3 What wavelength range would be most suitable for the photometric analysis of the indicator in a strongly basic medium?

4.4 What would be the absorbance of a 1.00×10^{-4} M (mol dm-3) solution of the indicator in alkaline form if measured at 545 nm in a 2.50 cm cell?

4.5 Solutions of the indicator were prepared in a strongly acidic solution (HCl, *pH* = 1) and in a strongly basic solution (NaOH, *pH* = 13). Perfectly linear relationships between absorbance and concentration were observed in both media at 490 nm and 625 nm, respectively.

The molar absorptivities at the two wavelengths are:

	λ = 490 nm	λ = 625 nm
HIn (HCl)	9.04×10^{2} M^{-1} cm^{-1}	3.52×10^{2} M^{-1} cm^{-1}
In- (NaOH)	1.08×10^{2} M^{-1} cm^{-1}	1.65×10^{3} M^{-1} cm^{-1}

(M = mol dm^{-3})

Calculate the absorbance (1.00 cm cell) at the two wavelengths for an aqueous 1.80×10^{-3} M (mol dm^{-3}) solution of the indicator HIn.

SOLUTION

4.1 The observed colour will be the complementary colour to that of the absorption maximum.

a) Acidic conditions (*pH* 1):

The sample absorbs at 490 ± 25 (blue-green) and thus will transmit the complementary colour and will appear to be yellow-orange (625 ± 25 nm).

b) Basic conditions (*pH* 13):

The sample absorbs at 625 ± 25 (yellow-orange) and thus will transmit the complementary colour and will appear to be blue-green (490 ± 25 nm).

4.2 The filter should transmit the colour that the sample will absorb most efficiently. The acidic sample absorbs most strongly in the blue range (490 ± 25 nm) and thus a similar colour filter would be most suitable for the photometric analysis of the sample.

4.3 The wavelength range to be used for maximum sensitivity should correspond to that at which the sample absorbs most strongly. The maximum absorbance for the basic form of the indicator in solution occurs at 625 ± 25 nm and this is the most suitable wavelength for the analysis.

4.4 From a graph of *A* versus wavelength, the absorbance of a 5.00×10^{-4} M basic solution at 545 nm is 0.256. From the plot, it is clear that this region of the graph is linear and thus the above value can also be interpolated from the data table.

$A = \varepsilon\, l\, c$ (Beer's Law)

where l = length of cell, c = concentration of analyte, ε = molar absorptivity.

Therefore $$\varepsilon = \frac{A}{l\,c} = \frac{0.256}{1.0\times 5.00\times10^{-4}} = 5.12\times10^{2}\ \text{M}^{-1}\ \text{cm}^{-1}$$

Absorbance of a 1.00×10^{-4} M basic solution of the indicator using a 2.50 cm cell is:

$A = 5.12\times10^{2}\times 2.50\times 1.0\times10^{-4} = 0.128$

4.5 The dissociation reaction of the indicator is:

[HIn] = [H+] + [In-]

accordingly,

$[H+] = [In-]$ (1)

and

$[HIn] + [In-] = 1.80\times10^{-3}$ M (2)

$$K_a = \frac{[H^+][In^-]}{[HIn]} \qquad (3)$$

Substitute (1) and (2) into (3)

$$K_a = \frac{[In^-]^2}{1.8\times10^{-3} - [In^-]} = 2.93\times10^{-5}$$

Rearrangement yields the quadratic expression

$[In-]^2 + 2.93\times10^{-5}\,[In-] - 5.27\times10^{-8} = 0$

which results in

$[In-] = 2.15\times10^{-4}$ M

$[HIn] = 1.80\times10^{-3}$ M – 2.15×10^{-4} M = 1.58×10^{-3} M

The absorbance at the two wavelengths are then:

$A_{490} = (9.04\times10^2 \times 1 \times 1.58\times10^{-3}) + (1.08\times10^2 \times 1 \times 2.15\times10^{-4}) = 1.45$

$A_{625} = (3.52\times10^2 \times 1 \times 1.58\times10^{-3}) + (1.65\times10^3 \times 1 \times 2.15\times10^{-4}) = 0.911$

PROBLEM 8

An electrolyte is prepared from H_2SO_4, $CuSO_4$ and distilled water and its volume is 100.0 cm^3. The concentrations of H+ and Cu^{2+} in the electrolyte are $c(H^+) = 1.000$ M (mol dm^{-3}) and $c(Cu^{2+}) = 1.000\times10^{-2}$ M (mol dm^{-3}), respectively. Two cubic platinum electrodes are immersed in the electrolyte. Both of the electrodes are single crystals with only one face (100) exposed to the electrolyte (the other five faces are blocked physically by an insulator which is stable in the electrolyte). The exposed surface area of each electrode is equal to 1.000 cm^2. During an electrolysis a total charge of 2.0000 C is passed between the cathode and the anode. At the cathode, two simultaneous processes are occurring: deposition of an epitaxial (layer-by-layer) Cu layer and H_2 gas generation. At the anode, O_2 gas is generated. The H_2 gas is collected in a flask under the following conditions (assume ideal gas behaviour):

$T = 273.15$ K and $P(H_2) = 1.01325\times10^4$ Pa; the volume of H_2 is equal to 2.0000 cm^3

8.1 Write equations of the processes taking place at the electrodes.

8.2 Calculate the number of moles of H_2 gas generated at the cathode and the number of moles of Cu deposited on the electrode.

8.3 Calculate the number of Cu monolayers formed on the Pt (100) cathode.

Note that the lattice constant of Pt is $a(Pt) = 3.9236\times10^{-8}$ cm.

Both Pt and Cu have the *fcc* (face centred cubic) crystallographic structure.

Molar masses and constants:

$M(H) = 1.00795$ g mol^{-1}

$M(Cu) = 63.546$ g mol^{-1}

$e = 1.60218\times10^{-19}$ C

$F = 96485.3$ C mol^{-1}

$R = 8.314510$ J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1}

$V_m = 22.4141$ dm^3

1 atm = 1.01325×10^5 Pa

$N_A = 6.02214\times10^{23}$ mol^{-1}

SOLUTION

Approach

- Determine the number of H_2 moles generated by the electrolysis.
- Calculate the charge required for the H_2 production and the charge of the formation of the Cu deposit and thus the number of moles of Cu in the deposit.
- Calculate the surface concentration of atoms in the Pt (100) face thus the number of Pt atoms per 1 cm^2; during an epitaxial growth the number of Cu atoms per 1 cm^2 equals the number of Pt atoms
- Determine the charge necessary to form one monolayer of Cu and subsequently the number of Cu monolayers on Pt (100)

Calculations

8.1 Balanced electrode equations

(a) Anode: $2\,H_2O \rightarrow H^+ + O_2 + 4\,e^-$

(b) Cathode:

Two reactions occur simultaneously at the cathode:

$2\,H^+ + 2\,e^- \rightarrow H_2$

$Cu^{2+} + 2\,e^- \rightarrow Cu$

8.2 Determination of the charge necessary to generate 2.0000 cm^3 of H_2 gas

(T = 273.15 K, p = 10.1325 kPa)

Two approaches to determination of the number of H_2 gas moles

(a) *Determination of n(H$_2$)*: $p\,V = n(H_2)\,R\,T$

$$n(H_2) = \frac{10132.5 \times 2.0000 \times 10^{-6}}{8.314510 \times 273.15} = 8.9230 \times 10^{-6}\ \text{mol}$$

$$n(H_2) = \frac{V(H_2)}{V_m}$$

V_m = 22.4141 dm^3 mol^{-1} (V_m refers to the pressure of 1 atm or at $p(H_2)$ = 101.325 kPa and because the pressure of H_2 is ten times smaller, one knows right away that the volume occupied under 1 atm would be 0.2000 cm^3)

$$n(H_2) = \frac{0.20000 \times 10^{-3}}{22.4141} = 8.9230 \times 10^{-6}\ \text{mol}$$

Determination of the charge necessary to generate 8.9230×10^{-6} moles of H_2 gas

Two approaches to determination of the charge:

(a) the number of H atoms, N_H, equals twice the number of H_2 molecules; if one multiplies N_H by e, then one gets the sought charge, Q_H

$$Q_H = 2 \times 8.9230\times10^{-6} \times N_A \times 1.60218\times10^{-19}$$

$$Q_H = 1.7219 \text{ C}$$

(b) one may use the Faraday law

$$m_H = k_H Q_H$$

where k_H is the electrochemical equivalent of H thus the mass of H generated by 1 C; to use this formula one has to calculate k_H; knowing that the charge of 1 F = 96485.3 C results in formation of 1 mole of H (1/2 mole of H_2), one may easily determine k_H

$$\frac{96485.3}{1.00795} = \frac{1.0000}{k_H}$$

$$k_H = 1.04467\times10^{-5} \text{ g C}^{-1}$$

Subsequently

$$Q_H = \frac{m_H}{k_H} = \frac{2\times 8.9230\times10^{-6}\times 1.00795}{1.04467\times10^{-5}}$$

$$Q_H = 1.7219 \text{ C}$$

Determination of the Cu deposition charge

$$Q_{Cu} = 2.0000 - Q_H$$

$$Q_{Cu} = 2.0000 - 1.7219 = 0.2781 \text{ C}$$

The moles of Cu is thus 0.2781 / 2 F = 1.4412×10^{-6}

8.3 Determination of the charge of formation of 1 monolayer (ML) of the Cu deposit and the number of Cu monolayers on the Pt (100) substrate

Calculate the number of surface Pt atoms in the (100) face

Surface area of the fundamental unit:

$$A_u = a_{Pt}^2 = 1.5395\times10^{-15} \text{ cm}^2$$

Number of atoms per fundamental (100) unit: $n_u = 2$

Surface atom concentration:

$$s_{Pt(100)} = \frac{n_u}{A_u} = \frac{2}{1.5395\times10^{-15}\,\text{cm}^2} = 1.2991\times10^{15}\,\text{cm}^{-2}$$

The number of Cu atoms per 1 cm^2 equals the number of Pt atoms - epitaxial growth

$$\sigma_{Cu(100)} = \sigma_{Pt(100)} = 1.2991\times10^{15}\,\text{cm}^{-2}$$

The charge of formation of one monolayer (ML) of Cu equals:

$$q_{ML} = 2\times e\times 1.2991\times10^{15}$$

$$q_{ML} = 4.1628\times10^{-4}\,\text{C}$$

Determination of the number of Cu monolayers on the Pt (100) substrate

$$n_{ML} = \frac{0.2780\text{C}}{4.1628\times10^{-4}\,\text{C}}$$

$$n_{ML} = 668\text{ ML}$$

One can also calculate the number of Cu atoms (8.6802×10^{17}) formed from the number of moles produced and divide this by the number of atoms (1.2991×10^{15}) on the exposed Pt surface to also arrive at 668 monolayers.

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5–14 JULY 1998, MELBOURNE, AUSTRALIA

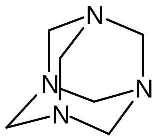
THEORETICAL PROBLEMS

PROBLEM 1

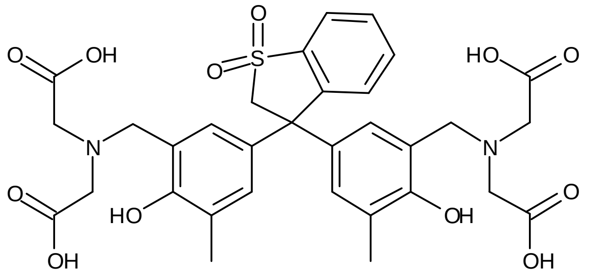
The following 8 steps describe the procedure for analysing a sample of alloy that contains both tin and lead.

1. A 0.4062 g sample of alloy was dissolved by heating it in a small beaker with a mixture of 11 M hydrochloric and 16 M nitric acid. The beaker was heated until the entire alloy dissolved. In this procedure, lead is oxidised to Pb(II) and tin becomes Sn(IV).
2. After 5 minutes of heating to expel oxides of nitrogen and chlorine, some acid remained. When the solution was cooled, a precipitate of some tin compounds and a lead compound appeared.
3. A 25.00 cm^3 aliquot of 0.2000 M Na_2H_2EDTA solution was added. The precipitate dissolved and a clear, colourless solution was obtained.
4. This solution was quantitatively transferred to a 250.0 cm^3 volumetric flask and made up to the mark with distilled water.
5. A 25.00 cm^3 aliquot of this solution was treated with 15 cm^3 of a 30 % w/v solution of hexamine (hexamethylenetetramine), some water and two drops of Xylenol Orange solution. The pH of each aliquot was 6.
6. The clear, yellow solution from Step 5 was titrated with standard 0.009970 M lead nitrate solution until the colour just changed from yellow to red. The titre at this endpoint was 24.05 cm^3.
7. 2.0 g of solid NaF was added to the titration flask. The solution turned back to yellow.
8. The solution was titrated with more standard 0.009970 M lead nitrate solution until the colour changed to red again. The titre at this endpoint was 15.00 cm^3.

Hexamine and Xylenol Orange have the structures shown below. The pK_b of hexamine is 9.5. Xylenol Orange is red below *pH* 4, yellow above *pH* 5.



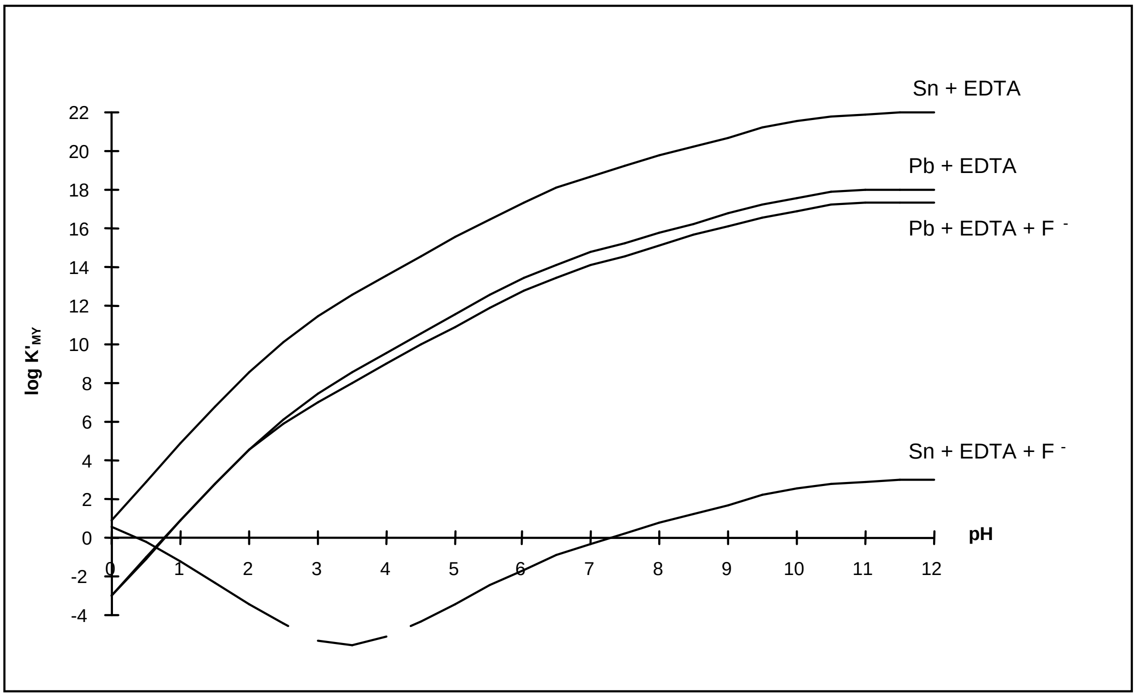
Hexamine



Xylenol Orange (XO)

K'_{MY} is the conditional formation constant = αK_{MY} .

K'_{MY} for the formation of the EDTA complexes of Pb(II) and Sn(IV), in the presence and absence of fluoride, are shown in the following Figure.



1.1 What is the lead compound that precipitates in Step 2?

1.2 Write a balanced ionic equation that explains the disappearance of the precipitate in Step 3 (at *pH* 6).

1.3 What is the purpose of hexamine in Step 5 of the analysis?

1.4 What is the purpose of Xylenol Orange in the analysis?

1.5 Write balanced ionic equations for the reactions occurring during the titration and responsible for the colour change at the endpoint in Step 6 of the analysis

1.6 What is the purpose of NaF in Step 7 of the analysis?

1.7 Write a balanced ionic equation for the reaction that occurs in Step 7.

1.8 Write a balanced ionic equation that explains why the colour changed from red to yellow in Step 7 of the analysis.

1.9 Write a balanced ionic equation that explains why the lines on the graph below of log K_{MY} *vs pH* for Pb + EDTA and Pb + EDTA + F^- are coincident below *pH* 2.

1.10 Calculate the percentage by weight of Sn and Pb in the alloy.

SOLUTION

1.1 $PbCl_2$ or any hydroxo species etc.

1.2 $PbCl_2(s) + H_2Y^{2-} \rightarrow PbY^{2-} + 2\ H^+ + 2\ Cl^-$ or similar

1.3 It forms a pH buffer.

1.4 It is a metallochromic indicator.

1.5 (i) The reaction that occurs during the titration:

$Pb^{2+} + H_2Y^{2-} \rightarrow PbY^{2-} + 2\ H^+$

(ii) At the endpoint, a slight excess of Pb^{2+} forms a red complex with the xylenol orange indicator:

Pb^{2+} + XO (yellow) $\rightarrow PbXO^{2+}$ (red)

1.6 The role of the NaF: It forms a complex with tin.

1.7 From the graph of log K'_{MY} ***vs*** *pH*, it can be seen that the fluoride forms a stable complex with Sn^{4+} but not with Pb^{2+} at *pH* 6, displacing EDTA:

$SnY + nF^- + 2\ H^+ \rightarrow SnF_n^{(n-4)-} + H_2Y^{2-}$ where n is typically 4 - 6.

1.8 The released EDTA destroys the small amount of red PbXO complex, producing free (yellow) XO. (Charge on XO ignored)

$H_2Y^{2-} + PbXO^{2+} \rightarrow PbY^{2-}$ + XO (yellow) + 2 H^+

1.9 Below *pH* 2, F^- is protonated and does not compete effectively with Y for Pb^{2+}

$H^+ + F^- \rightarrow HF$.

1.10 The percentage by mass of Sn and Pb in the alloy:

The amount of EDTA in excess from the amount of standard Pb^{2+} titrant:

$n(\text{EDTA}) = n(Pb^{2+}) = 0.02405\ dm^3 \times 0.009970\ mol\ dm^{-3} = 2.398 \times 10^{-4}$ mol.

The original amount of EDTA:

$n(\text{EDTA}_{)\text{init.}} = 0.1 \times 25.00 \text{ dm}^3 \times 0.2000 \text{ mol dm}^{-3} = 5.000 \times 10^{-4}$ mol

EDTA consumed by the Pb^{2+} and Sn^{4+} in a 25 cm^3 aliquot:

$n(\text{EDTA})_{\text{consumed}} = 5.000 \times 10^{-4} - 2.398 \times 10^{-4} \text{ mol} = 2.602 \times 10^{-4} \text{ mol} = n(Pb^{2+} + Sn^{4+})$ in a 25 cm^3 aliquot.

The amount of EDTA released from SnY by reaction with fluoride:

$n(\text{EDTA})_{\text{ released}} = n(Pb^{2+})_{\text{stand.}} = 15.00 \text{ cm}^3 \times 0.009970 \text{ mol dm}^{-3} = 1.496 \times 10^{-4}$ mol =

= $n(Sn^{4+})$ in the 25 cm^3 aliquot

in a 25 cm^3 aliquot $n(Pb^{2+}) = (2.602 \times 10^{-4} - 1.496 \times 10^{-4}) \text{ mol} = 1.106 \times 10^{-4}$ mol

In the original 0.4062 g sample of alloy:

$m(\text{Sn}) = 10 \times 1.496 \times 10^{-4} \text{ mol} \times 118.69 \text{ g mol}^{-1} = 0.1776$ g

$m(\text{Pb}) = 10 \times 1.106 \times 10^{-4} \text{ mol} \times 207.19 \text{ g mol}^{-1} = 0.2292$ g

The percentages of tin and lead:

Sn: $100 \times (0.1776 / 0.4062) = 43.7$ %

Pb: $100 \times (0.2292 / 0.4062) = 56.4$ %

PROBLEM 5

Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to $[Au(CN)_2]^-$, which is soluble in water (reaction 1).

After equilibrium has been reached, the aqueous phase is pumped off and the metallic gold is recovered from it by reacting the gold complex with zinc, which is converted to $[Zn(CN)_4]^{2-}$ (reaction 2).

5.1 Write balanced ionic equations for reactions (1) and (2).

Gold in nature is frequently alloyed with silver which is also oxidized by aerated sodium cyanide solution.

5.2 Five hundred litres (500 L) of a solution 0.0100 M in $[Au(CN)_2]^-$ and 0.0030 M in $[Ag(CN)_2]^-$ was evaporated to one third of the original volume and was treated with zinc (40 g). Assuming that deviation from standard conditions is unimportant and that all these redox reactions go essentially to completion, calculate the concentrations of $[Au(CN)_2]^-$ and of $[Ag(CN)_2]^-$ after reaction has ceased.

$[Zn(CN)_4]^{2-} + 2\ e^- \rightarrow Zn + 4\ CN^-$ $\quad E° = -1.26$ V

$[Au(CN)_2]^- + e^- \rightarrow Au + 2\ CN^-$ $\quad E° = -0.60$ V

$[Ag(CN)_2]^- + e^- \rightarrow Ag + 2\ CN^-$ $\quad E° = -0.31$ V

5.3 $[Au(CN)_2]^-$ is a very stable complex under certain conditions. What concentration of sodium cyanide is required to keep 99 mol% of the gold in solution in the form of the cyanide complex? $\{[Au(CN)_2]^- : K_f = 4 \times 10^{28}\}$

5.4 There have been several efforts to develop alternative gold extraction processes which could replace this one. Why? Choose one of the options on the answer sheet.

SOLUTION

5.1 Reaction 1:

$4\ Au + 8\ CN^- + O_2 + 2\ H_2O \rightarrow 4\ [Au(CN)_2]^- + 4\ OH^-$

reaction 2:

$Zn + 2\,[Au(CN)_2]^- \rightarrow [Zn(CN)_4]^{2-} + 2\,Au$

5.2 $E^0(Ag/Zn) = -0.31 - (-1.26) = 0.95$ V

$E^0(Au/Zn) = -0.60 - (-1.26) = 0.66$ V

$E^0(Ag/Zn) > E^0(Au/Zn)$

Therefore the Ag(I) complex will be reduced first.

(i) mol Ag(I) in 500 dm^3 = 500 × 0.0030 = 1.5 mol

(ii) mol Au(I) in 500 dm^3 = 500 × 0.010 = 5.0 mol

(iii) mol Zn in 40 g = 40 / 65.38 = 0.61 mol

1 mol zinc reacts with 2 mol of Ag(I) or Au(I)

Therefore 0.61 mol Zn will consume 1.2 mol $[Ag(CN)_2]^-$

$[Ag(CN)_2]^-$ remaining = 1.5 – 1.2 = 0.3 mol

$[Au(CN)_2]^-$ will not be reduced.

Concentration of $[Au(CN)_2]^-$ when reaction has ceased = 0.010 × 3 = 0.030 M

Concentration of $[Ag(CN)_2]^-$ when reaction has ceased = 0.3 × (3 / 500) = 0.002 M

$[Zn(CN)_4]^{2-} + 2\,e^- \rightarrow Zn + 4\,CN^-$ $E^0 = -1.26$ V

$[Au(CN)_2]" + e^- \rightarrow Au + 2CN\sim$ $E^0 = -0.60$ V

$[Ag(CN)_2]" + e^- \rightarrow Ag + 2CN-$ $E^0 = -0.31$ V

5.3 $Au^+ + 2\,CN^- \rightarrow [Au(CN)_2]^-$ $K_f = 4\times10^{28}$

99 mol % $[Au(CN)_2]^-$

$$K_f = \frac{[Au(CN)_2^-]}{[Au^+]\,[CN^-]^2}$$

$$\frac{[Au(CN)_2^-]}{[Au^+] + [Au(CN)_2^-]} = 99/100$$

Thus: $100 \times [Au(CN)_2^-] = 99 \times [Au^+] + 99 \times [Au(CN)_2^-]$

Therefore $[Au^+] = [Au(CN)_2^-]\ /\ 99$

Substituting into K_f:

4×10^{28} = 99 / [CN"]^2

[CN^-] = 5×10^{-14}

5.4 Sodium cyanide escapes into ground water and produces hydrogen cyanide which is toxic to many animals.

PROBLEM 2

PART A

A diprotic acid , H_2A , undergoes the following dissociation reactions :

$$H_2A \rightleftharpoons HA^- + H^+; \qquad K_1 = 4.50\times10^{-7}$$

$$HA^- \rightleftharpoons A^{2-} + H^+; \qquad K_2 = 4.70\times10^{-11}$$

A 20.00 cm^3 aliquot of a solution containing a mixture of Na_2A and NaHA is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode *pH* meter. Two points on the titration curve are as follows :

cm^3 HCl added	*pH*
1.00	10.33
10.00	8.34

2.1 On adding 1.00 cm^3 of HCl, which species reacts first and what would be the product?

2.2 What is the amount (mmol) of the product formed in (2.1)?

2.3 Write down the main equilibrium of the product from (2.1) reacting with the solvent?

2.4 What are the amounts (mmol) of Na_2A and NaHA initially present?

2.5 Calculate the total volume of HCl required to reach the second equivalence point.

PART B

Solutions I, II and III contain a *pH* indicator HIn (K_{In} = 4.19×10^{-4}) and other reagents as indicated in the table. The absorbance values at 400 nm of the solutions measured in the same cell, are also given in the table. K_a of CH_3COOH is 1.75×10^{-5}.

Table:

	Solution I	Solution II	Solution III
Total concentration of indicator HIn	1.00×10^{-5} M	1.00×10^{-5} M	1.00×10^{-5} M
Other reagents	1.00 M HCl	0.100 M NaOH	1.00 M CH_3COOH
Absorbance at 400	0.000	0.300	?

2.6 Calculate the absorbance at 400 nm of solution III.

2.7 Apart from H_2O, H^+ and OH^-, what are all the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio?

2.8 What is the absorbance at 400 nm of the solution in (2.7)?

2.9 What is the transmittance at 400 nm of the solution in (2.7)?

SOLUTION

PART A

2.1 Species which reacts first is A^{2-}.

The product is HA^-.

2.2 n(product) = 1.00 × 0.300 = 0.300 mmol

2.3 $HA^- + H_2O \rightleftharpoons H_2A + OH^-$

2.4 At pH 8.34 which is equal to $(pK_{a1} + pK_{a2}) / 2$ all A^- are protonated as HA^- .

Therefore $n(A^{2-})$ initially present in the solution = 0.300 × 10.00 = 3.00 mmol

At pH = 10.33, the system is a buffer in which the ratio of $[A^{2-}]$ and $[HA^-]$ is equal to 1.

Thus

$[HA^-]_{initial} + [HA^-]_{formed} = [A^{2-}]_{jnitial} - [HA^-]_{formed}$

$n(HA^-)_{initial}$ = 3.00 – 0.300 – 0.300 mmol = 2.40 mmol

$n(Na_2A)$ = <u>3.00 mmol</u>

n(NaHA) = <u>2.40 mmol</u>

2.5 Total volume of HCl required = [(2 × 3.00) + 2.40] / 0.300 = 28.00 cm^3

PART B

2.6 Solution III is the indicator solution at 1×10^{-5} M in a solution containing 1.0 M CH_3COOH.

To obtain the absorbance of the solution, it is necessary to calculate the concentration of the basic form of the indicator which is dependent on the [H$^+$] of the solution.

[H$^+$] of solution III = $\sqrt{K_a c} = \sqrt{1.75\times10^{-5}\times1.0} = 4.18\times10^{-3}$

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]} = \frac{1\times10^{-3.38}}{1\times10^{-2.38}} = 0.100$$

Since $[\text{HIn}] + [\text{In}^-] = 1\times10^{-5}$

$10\,[\text{In}^-] + [\text{In}^-] = 1\times10^{-5}$

$[\text{In}^-] = 0.091\times10^{-5}$

Absorbance of solution III = $\dfrac{0.091\times10^{-5}}{1.00\times10^{-5}}\times0.300 = 0.027$

2.7 All the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio (apart from H^+, OH^- and H_2O) are the following: CH_3COOH , CH_3COO^-, Na^+ , HIn , In^-.

2.8 When solutions II and III are mixed at 1 : 1 volume ratio, a buffer solution of 0.05 M CH_3COO^- / 0.45 M CH_3COOH is obtained.

[H$^+$] of the mixture solution = $K_a\dfrac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.75\times10^{-5}\times\dfrac{0.45}{0.05} = 15.75\times10^{-5}$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]} = \frac{1\times10^{-3.38}}{15.75\times10^{-5}} = 2.65$$

Since $[\text{HIn}] + [\text{In}^-] = 1\times10^{-5}$

$\dfrac{[\text{In}^-]}{2.65} + [\text{In}^-] = 1\times10^{-5}$

$[\text{In}^-] = 0.726\times10^{-5}$

Absorbance of solution = $\dfrac{0.726\times10^{-5}}{1.00\times10^{-5}}\times0.300 = 0.218$

2-9 Transmittance of solution = $10^{-0.218} = 0.605 \Rightarrow 60.5\%$

PROBLEM 6

Hard Water

In Denmark the subsoil consists mainly of limestone. In contact with ground water containing carbon dioxide some of the calcium carbonate dissolves as calcium hydrogen carbonate. As a result, such ground water is hard, and when used as tap water the high content of calcium hydrogen carbonate causes problems due to precipitation of calcium carbonate in, for example, kitchen and bathroom environments.

Carbon dioxide, CO_2, is a diprotic acid in aqueous solution. The pK_a-values at 0 ℃ are:

$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ pK_{a1} = 6.630

$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$ pK_{a2} = 10.640

The liquid volume change associated with dissolution of CO_2 may be neglected for all of the following problems. The temperature is to be taken as being 0 ℃.

6.1 The total concentration of carbon dioxide in water which is saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar is 0.0752 mol dm^{-3}. Calculate the volume of carbon dioxide gas which can be dissolved in one litre of water under these conditions.

The gas constant $R = 8.314$ J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

6.2 Calculate the equilibrium concentration of hydrogen ions and the equilibrium concentration of CO_2 in water saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.3 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium hydrogen carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.4 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar. Ignore water dissociation effects.

6.5 The solubility of calcium carbonate in water at 0 °C is 0.0012 g per 100 cm3 of water. Calculate the concentration of calcium ions in a saturated solution of calcium carbonate in water.

The hard groundwater in Denmark is formed via contact of water with limestone in the subsoil which reacts with carbon dioxide dissolved in the groundwater according to the equilibrium equation:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\,HCO_3^{-}(aq)$$

The equilibrium constant, K, for this reaction is $10^{-4.25}$ at 0 °C.

6.6 Calculate the concentration of calcium ions in water in equilibrium with calcium carbonate in an atmosphere with a partial pressure of carbon dioxide of 1.00 bar.

6.7 A 0.0150 M solution of calcium hydroxide is saturated with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the solution by considering the equilibrium equation given above in connection with problem 6.6.

6.8 The calcium hydroxide solution referred to in problem 6.7 is diluted to twice the volume with water before saturation with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the resulting solution saturated with CO_2.

6.9 Calculate the solubility product constant for calcium carbonate from the data given above.

SOLUTION

6.1 $c(CO_2) = 0.0752$ M $n(CO_2) = 0.0752$ mol

The ideal gas equation: $p\,V = n\,R\,T$

$1.00 \text{ bar} \times V = 0.0752 \text{ mol} \times 0.08314 \text{ dm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}$

$V = 1.71 \text{ dm}^3$

6.2 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$[H^+] = [HCO_3^-] = x$ and $[CO_2] + [HCO_3^-] = 0.0752$

$$K_a = 10^{-6.63} = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} = \frac{x^2}{0.0752 - x}$$

$[H^+] = 0.000133$ and $[CO_2] = 0.0751$

6.3 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$[CO_2] = 0.0751$ and $[HCO_3^-] = 0.0100$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x\ 0.0100}{0.0751}$$

$\underline{x = [H^+] = 1.76\times10^{-6}}$

6.4 $CO_2(aq) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2\ HCO_3^-(aq)$ $[HCO_3^-] = 0.0200$

$CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x\ 0.0200}{0.0751}$$

$x = [H^+] = 8.8\times10^{-7}$

6.5 0.0012 g $CaCO_3$ in 100 cm^3 of water

0.0012 g /100 × 0872 g mol^{-1} = 0.000012 mol $CaCO_3$ in 100 cm^3 of water

$[Ca^{2+}] = 1.2\times10^{-4}$ $c(Ca^{2+}) = 1.2\times10^{-4}$ mol dm^{-3}

6.6 $K = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = 10^{-4.25}$ and $2\,[Ca^{2+}] = [HCO_3^-]$

$\frac{4\,[Ca^{2+}]}{0.0751} = 10^{-4.25}$ $[Ca^{2+}] = 1.02\times10^{-2}$ $c(Ca^{2+}) = 1.02\times10^{-2}$ mol dm^{-3}

6.7 $c(Ca(OH)_2) = 0.015$ mol dm^{-3}

$OH^-(aq) + CO_2(aq) \rightarrow HCO_3^-(aq)$

All hydroxide has been consumed ($K = 10^{7.37}$).

From problem 6.6 we found that the maximum possible calcium ion concentration is smaller, *i.e.* precipitation of $CaCO_3$

$[Ca^{2+}] = 1.02\times10^{-2}$ $c(Ca^{2+}) = 1.02\times10^{-2}$ mol dm^{-3}

6.8 $c(Ca(OH)_2) = 0.0075$ mol dm^{-3}

From problem 6.6 we found that the maximum possible calcium ion concentration we can have, is 1.02×10^{-2} mol dm^{-3}, *i.e.* no precipitation of $CaCO_3$ occurs.

$[Ca^{2+}] = 0.75\times10^{-2}$ $c(Ca^{2+}) = 0.75\times10^{-2}$ mol dm^{-3}

6.9

$$K = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} \times \frac{[CO_3^{2-}][H^+]}{[CO_3^{2-}][H^+]} = \frac{K_{sp}\,K_{a1}}{K_{a2}}$$

$$K_{sp} = 10^{-8.26}$$

PROBLEM 2

Phosphoric Acid

Phosphoric acid is of a great importance in fertilizer industry. Besides, phosphoric acid and its various salts have a n umber of applications in metal treatment, food, detergent and toothpaste industries.

2.1 The pK values of the three successive dissociations of phosphoric acid at 25 °C are:

pK_{1a} = 2.12

pK_{2a} = 7.21

pK_{3a} = 12.32

Write down the conjugate base of dihydrogen phosphate ion and determine its pK_b value.

Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and root beers. A cola having a density of 1.00 g cm^{-3} contains 0.05 % by weight of phosphoric acid.

2.2 Determine the *pH* of the cola (ignoring the second and the third dissociation steps for phosphoric acid). Assume that the acidity of the cola arises only from phosphoric acid.

2.3 Phosphoric acid is used as a fertiliser for agriculture. 1.00×10^{-3} M phosphoric acid is added to an aqueous soil suspension and the *pH* is found to be 7.00.

Determine the fractional concentrations of all the different phosphate species present in the solution. Assume that no component of the soil interacts with any phosphate species.

2.4 Zinc is an essential micronutrient for plant growth. Plant can absorb zinc in water soluble form only. In a given soil water with *pH* = 7.0, zinc phosphate was found to be the only source of zinc and phosphate. Calculate the concentration of [Zn^{2+}] and [PO_4^{3-}] ions in the solution. Ksp for zinc phosphate is 9.1×10^{-33}.

SOLUTION

2.1 The conjugate base of dihydrogen phosphate ($H_2PO_4^-$) is monohydrogen phosphate (HPO_4^{2-}) :

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ K_{2a}

$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ K_{2b}

$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$ K_w

$pK_{2a} + pK_{2b} = pK_w = 14$

$pK_{2b} = 6.79$

2.2 Concentration of $H_3PO_4 = \dfrac{0.5}{98} = 0.0051$ M

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$

0.0051-x x + x

$pK_{1a} = 2.12$ gives $K_{1a} = 7.59\times10^{-3}$

$$7.59\times10^{-3} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = \frac{x^2}{0.0051 - x}$$

$x = [H_3O^+] = 3.49\times10^{-3}$

$pH = 2.46$

2.3 Let $f_0 = \dfrac{[H_3X]}{C}$, $f_1 = \dfrac{[H_2X^-]}{C}$,

$f_2 = \dfrac{[HX^{2-}]}{C}$ and $f_3 = \dfrac{[X^{3-}]}{C}$

denote the fractional concentrations of different phosphate species. C is the total initial concentration of H_3X. ($X = PO_4$)

$f_0 + f_1 + f_2 + f_3 = 1$

$$K_{1a} = \frac{[H_2X^-][H_3O^+]}{[H_3X]} = \frac{f_1}{f_0}[H_3O^+]$$

$$K_{2a} = \frac{[HX^{2-}][H_3O^+]}{[H_2X^-]} = \frac{f_2}{f_1}[H_3O^+]$$

$$K_{3a} = \frac{[X^{3-}][H_3O^+]}{[HX^{2-}]} = \frac{f_3}{f_2}[H_3O^+]$$

These equations lead to

$$f_0 = \frac{[H_3O^+]^3}{D}, \qquad f_1 = \frac{K_{1a}[H_3O^+]^2}{D}, \qquad f_2 = \frac{K_{1a}K_{2a}[H_3O^+]}{D}, \qquad f_3 = \frac{K_{1a}K_{2a}K_{3a}}{D}$$

where D = $K_{1a}\ K_{2a}\ K_{3a} + K_{1a}\ K_{2a}\ [H_3O^+] + K_{1a}\ [H_3O^+]^2 + [H_3O^+]^3$

From the values of pK_{1a}, pK_{2a}, pK_{3a} and pH one gets

$K_{1a} = 7.59\times10^{-3}$; $K_{2a} = 6.17\times10^{-8}$; $K_{3a} = 4.79\times10^{-13}$; $[H_3O^+] = 1\times10^{-7}$

The fractional concentrations of different phosphate species are:

H_3PO_4 $(f_0) = 8.10\times10^{-6}$

$H_2PO_4^-$ $(f_1) = 0.618$

HPO_4^{2-} $(f_2) = 0.382$

PO_4^{3-} $(f_3) = 1.83\times10^{-6}$

2.4 Let S (mol dm^{-3}) be the solubility of $Zn_3(PO_4)_2$ in soil water.

$[Zn^{2+}] = 3\ S$

Total concentration of different phosphate species = 2 S

$[PO_4^{3-}] = f_3 \times 2\ S$

f_3 can be determined from the relation derived in **2.3**

For $pH = 7$, $f_3 = 1.83\times10^{-6}$

$K_{sp} = [Zn^{2+}]^3\ [PO_4^{3-}]^2$

$9.1\times10^{-33} = (3\ S)^3\ (f_3 \times 2\ S)^2$

$[Zn^{2+}] = 9\times10^{-5}$

$[PO_4^{3-}] = 1.1\times10^{-10}$

Solubility of $Zn_3(PO_4)_2 = 3.0\times10^{-5}$ mol dm^{-3}

PROBLEM 2

Nitrogen Cycle in Nature

Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of NH_3 first to nitrite and then to nitrate, the storage form of nitrogen in the soil.

$$NH_3 + 2\,O_2 + NADH \xrightarrow[\textit{bacteria}]{\textit{Nitrosomonas}} NO_2^- + 2\,H_2O + NAD^+$$

NADH is the biochemical reducing agent of the coenzyme nicotinamide dinucleotide (NAD), NAD^+ is the oxidized form of the coenzyme NAD.

$$2\,NO_2^- + O_2 \xrightarrow[\textit{bacteria}]{\textit{Nitrobacter}} 2\,NO_3^-$$

2.1 Give the oxidation states of N in the following series: (Use the boxes below the compounds)

$$\begin{array}{ccccc} NH_3 & \longrightarrow & NO_2^- & \longrightarrow & NO_3^- \\ \boxed{} & & \boxed{} & & \boxed{} \end{array}$$

The spectrophotometric analysis of nitrite is based on a reaction with an indicator. The coloured product then obtained has an absorbance maximum at λ = 543 nm. For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength λ = 543 nm is plotted against nitrite concentration in a series of standards.

2.2 The measurements are performed at the wavelength with the maximum absorbance because:

☐ There is no interference of impurities.

☐ There is no contribution of stray light.

☐ There is optimal accuracy of the measurement.

☐ None of these statements.

Mark the correct answer.

The absorption is measured with a single beam spectrophotometer. However 5 % of the light, the so-called stray light I_s, strikes the detector directly (see Figure 2).

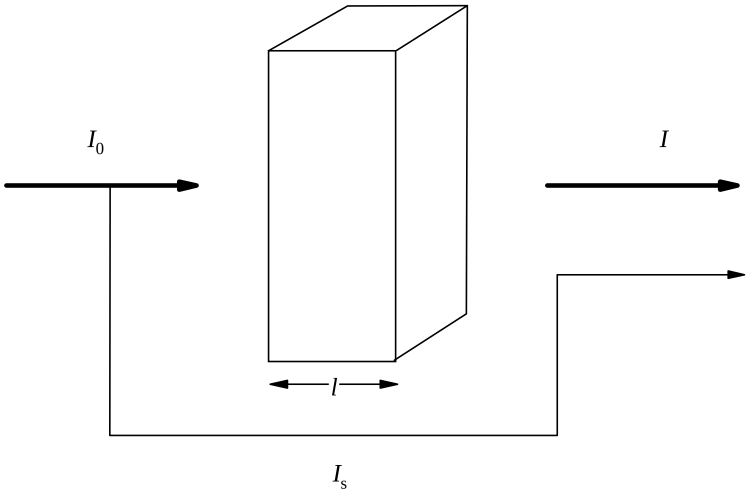


Figure 2

2.3 Calculate the value of the absorbance *A* shown by the spectrophotometer if ε = 6 000 M^{-1} cm^{-1}, *l* = 1 cm and *c* = 1×10^{-4} M

For a nitrite determination in water the following data have been measured.

Table 1

concentration of nitrite nitrogen (ppm)	absorbance at 543 nm (1.000 cm cell)
blank	0.003 (due to impurities in the solvent)
0.915	0.167
1.830	0.328

2.4 Determine (show calculation) from the data given above, using the values corrected for the solvent impurities, the slope m and the intercept b of the calibration curve *A* = *m c* + b.

The duplicate analyses of a water sample are given below. The measurements have been performed at a wavelength of 543 nm and in a 2.000 cm cell.

Table 2

water sample	absorbance
analysis 1	0.562
analysis 2	0.554

For the calculation of the concentration of the nitrite nitrogen (c in ppm) the equation obtained by the method of least squares

$$\text{corrected absorbance} = 0.1769\ c + 0.0015 \qquad \text{(a)}$$

may be applied, using the measurements in a 1.000 cm cell.

2.5 Calculate the average nitrite nitrogen concentration in ppm and μg cm^{-3}.

Hint: Take the blank from problem 2.4.

SOLUTION

2.1 NH_3: –III (–3) NO_2^-: III (3) NO_3^-: V (5)

2.2 Correct answer: There is optimal accuracy of the measurement.

2.3 $I_S = 0.05 \times I_0$ $A = \log \dfrac{I_0}{I + I_S}$ (see Figure 2)

The absorption of the solution A_{sol} is given by the relation:

$$A_{sol} = \log\ 0.95 \times \frac{I_0}{I} = \varepsilon\, c\, d$$

$$I = 0.95 \times I_0 \times 10^{-6000 \cdot 0.0001 \cdot 1} = 0.95\ I_0 \times 10^{-0.6}$$

$$A = \log \frac{I_0}{0.95 \times I_0 \times 10^{-0.6} + 0.05 \times I_0} = 0.54$$

2.4 The absorbance of the blank solution (see Table): $A = 0.003$.

Slope m of the calibration curve:

$$m = \frac{\Delta A}{\Delta c} = \frac{A_2 - A_1}{c_2 - c_1} = \frac{0.325 - 0.164}{1.830 - 0.915} = \frac{0.161}{0.915\ \text{M}} = 0.176\ \text{M}^{-1}$$

Note: Corrected absorbance values were used in the calculation.

$A = 0.176\ c + \text{b}$

For $c = 0$, $A = 0.003$.

Thus: b = 0.003

2.5 The average absorption in a 2 cm cell is 0.558; thus, in a 1 cm cell is 0.279.

Regarding the blank value (0.003) the corrected absorption has the value 0.276.

Substituting this value into the equation (a) gives:

$$c = \frac{0.276 - 0.0015}{0.1769}\ \text{ppm}$$

$$c = 1.55\ \text{ppm} = 1.55\ \mu\text{g cm}^{-3}$$

PROBLEM 8

Colloids

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest.

(T = 298.15 K throughout whole problem)

Solution **A** is an aqueous solution of $CaCl_2$ with a concentration of 1.780 g dm^{-3}. Solution **B** is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g dm^{-3}.

$pK_{a1}(H_2CO_3) = 6.37$ $\quad$ $pK_{a2}(HCO_3^-) = 10.33$

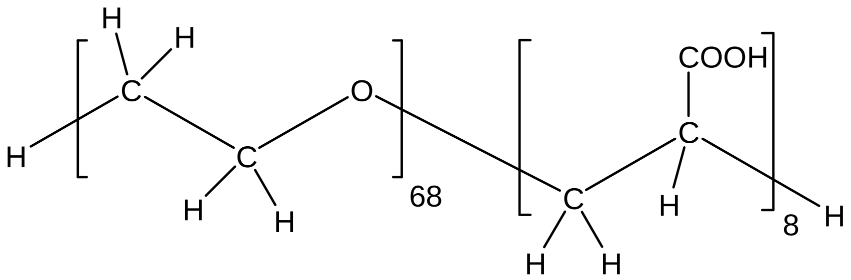
8.1 Calculate the *pH* of solution **B** using reasonable assumptions.

100 cm^3 of solution **A** and 100 cm^3 of solution **B** are mixed to form solution **C**. Solution **C** is adjusted to *pH* 10. A precipitate forms.

$K_{sp}(Ca(OH)_2) = 6.46\times10^{-6}$ $\quad$ $K_{sp}(CaCO_3) = 3.31\times10^{-9}$

8.2 Show by calculation for each of the compounds $Ca(OH)_2$ and $CaCO_3$ whether it can be found in the precipitate or not.

In a similar experiment 100 cm^3 of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (**A**+**B**) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

8.3 Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 cm^3 of an aqueous NaOH solution (c(NaOH) = 0.19 mol dm^{-3}). The solution is diluted by the addition of 200 cm^3 of water. Assume that the new solution contains only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a *pH* of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be $M = 8.01 \cdot 10^8$ g mol^{-1}
- The charge of the particles is found to be Z = –800 (number of unit charges).
  (pK_a(COOH, copolymer) = 4.88)

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

8.5 Calculate which modification of calcium carbonate has been formed.

Modification	density
Calcite	2.71 g cm^{-3}
Vaterite	2.54 g cm^{-3}
Aragonite	2.95 g cm^{-3}

SOLUTION

8.1 pH of solution **B**:

$$K_{b2} = \frac{c(\mathrm{HCO_3^-})/(1\,\mathrm{mol\,dm^{-3}}) \times c(\mathrm{OH^-})/(1\,\mathrm{mol\,dm^{-3}})}{c(\mathrm{CO_3^{2-}})/(1\,\mathrm{mol\,dm^{-3}})} \qquad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

$$K_{b2} = 2.14\times10^{-4}$$

$K_{b1} = 2.34\times10^{-8}$

Since $K_{b2} >> K_{b1}$, only one protonation step of the $\mathrm{CO_3^{2-}}$ has to be considered.

$c(HCO_3^-) = c(OH^-) = x$ and $c(CO_3^{2-}) = c_0(CO_3^{2-}) - x$

$$c_0(Na_2CO_3) = \frac{1.700 \text{ g dm}^{-3}}{105.99 \text{ g mol}^{-1}}$$

$c_0(Na_2CO_3) = c_0(CO_3^{2-}) = 0.016 \text{ mol dm}^{-3}$

$$K_{b2} = \frac{x^2/(1 \text{ mol dm}^{-3})}{(c_0(CO_3^{2-}) - x)} \qquad x = c(OH^-) = 1.75\times10^{-3} \text{ mol dm}^{-3}$$

$pH = 11.2$

8.2 $Ca(OH)_2$, $CaCO_3$ in the precipitate?

$M(CaCl_2) = 110.98 \text{ g mol}^{-1}$ $pH = 10$, $c(OH^-) = 1\times10^{-4} \text{ mol dm}^{-3}$

$$c_0(Na_2CO_3) = \frac{1.700 \text{ g cm}^{-3}}{105.99 \text{ g mol}^{-1} \times 2} \qquad c(CaCl_2) = \frac{1.780 \text{ g dm}^{-3}}{110.98 \text{ g mol}^{-1} \times 2}$$

$c_0(Na_2CO_3) = 8.0\times10^{-3} \text{ mol dm}^{-3}$ $c(CaCl_2) = c_0(Ca^{2+}) = 8.0\times10^{-3} \text{ mol dm}^{-3}$

Calculations for $Ca(OH)_2$:

$c(OH^-)^2 \times c_0(Ca^{2+}) = 8\times10^{-11} < 6.46\times10^{-6} = K_{sp}(Ca(OH)_2)$ no precipitate

Calculations for $CaCO_3$:

$$K_{b2} = \frac{c(HCO_3^-)\times c(OH^-)}{c(CO_3^{2-})}, \qquad c(HCO_3^-) = \frac{K_{b2}}{c(OH^-)} \times c(CO_3^{2-})$$

$c(HCO_3^-) = 2.14 \times c(CO_3^{2-})$ and $c(HCO_3^-) + c(CO_3^{2-}) = c_0(Na_2CO_3)$

$2.14 \times c(CO_3^{2-}) + c(CO_3^{2-}) = 8.0\times10^{-3} \text{ mol dm}^{-3}$

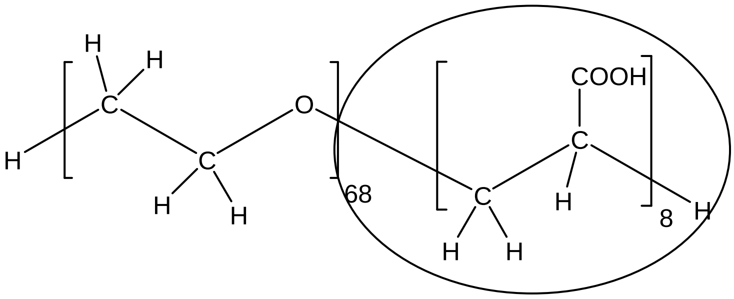
Initial concentration of CO_3^{2-} in solution **C**: $c(CO_3^{2-}) = 2.55\times10^{-3} \text{ mol dm}^{-3}$

Initial concentration of Ca^{2+} in solution **C**: $c(Ca^{2+}) = 8.0\times10^{-3} \text{ mol dm}^{-3}$

hence $c(\mathrm{CO_3^{2-}}) \times c(\mathrm{Ca^{2+}}) = 2.04\times10^{-5} > 3.3\times10^{-9} = K_{sp}(\mathrm{CaCO_3})$ precipitate

$Ca(OH)_2$	will be found in the precipitate	yes ☐	no ☒
$CaCO_3$	will be found in the precipitate	yes ☒	no ☐

8.3 Circle the block that attaches to the $CaCO_3$ crystal:



Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

$$\mathrm{RCOOH + OH^- \rightleftarrows RCOO^- + H_2O} \qquad pK_b = 9.12$$

pH and pK_a lead to the total concentration of COOH groups in the solution:

$c(\mathrm{COO^-}) = x$ $\qquad c(\mathrm{COOH}) = c_0(\mathrm{COOH}) - x$ $\qquad x = c_0(\mathrm{OH^-}) - c(\mathrm{OH^-})$

$$c_0(\mathrm{OH^-}) = \frac{50\ \mathrm{cm^3}}{250\ \mathrm{cm^3}}\ 0.19\ \mathrm{mol\ dm^{-3}} \qquad c_0(\mathrm{OH^-}) = 0.038\ \mathrm{mol\ dm^{-3}}$$

$$c(\mathrm{OH^-}) = 10^{-1.7}\ \mathrm{mol\ dm^{-3}} = 0.02\ \mathrm{mol\ dm^{-3}} \qquad x = 0.018\ \mathrm{mol\ dm^{-3}}$$

$$K_b = \frac{(c_0(\mathrm{COOH})\ \text{-x}) / (1\ \mathrm{mol\ dm^{-3}}) \times c(\mathrm{OH^-}) / (1\ \mathrm{mol\ dm^{-3}})}{\mathrm{x} / (1\ \mathrm{mol\ dm^{-3}})}$$

$$c_0(\text{COOH}) = \frac{K_b\ \text{x} \times (1\ \text{mol dm}^{-3})}{c(\text{OH}^-)} + \text{x}$$

$$c_0(\text{COOH}) = \left(\frac{0.018 \times 10^{-9.12}}{0.02} + 0.018\right) \text{mol dm}^{-3}$$

$c_0(\text{COOH}) = 0.018\ \text{mol dm}^{-3}$

(Or as pH >> pK_a : $c_0(\text{COOH}) = c(\text{COOH}) + \ \text{x} \approx \text{x}$)

To*tal concentration of polymer chains* $c(\text{polymer}) = \dfrac{c_0(\text{COOH})}{8}$

$M(\text{polymer}) = M(\text{C}_{160}\text{O}_{84}\text{H}_{306}) = 3574.66\ \text{g mol}^{-1}$

$m(\text{polymer}) = c(\text{polymer}) \times V \times M(\text{polymer})$

$$m(\text{polymer}) = \frac{c_0(\text{COOH}) \times V \times M(\text{polymer})}{8} = \frac{0.018 \times 0.250 \times 3574.66}{8}\text{g} = 2.0\ \text{g}$$

8.5 Modification of $CaCO_3$:

The charge of the particles is caused by the number of protolized COOH groups per particle.

$c(\text{COO}^-) \approx c_0(\text{COOH})$, $\alpha \approx 1$

Number of COOH groups per particle: $N_{\text{COOH}} = \dfrac{|Z|}{\alpha}$ $N_{\text{COOH}} = 800$

Number of polymer chains per particle: $N_{\text{polymer}} = \dfrac{N_{\text{COOH}}}{8} = 100$

The number of polymers per particle indicates the mass of polymer per particle. Thus, the mass of the calcium carbonate particle can be calculated:

$M(\text{CaCO}_3\ \text{particle}) = M(\text{total particle}) - N_{\text{polymer}}\ M(\text{polymer})$

$M(\text{CaCO}_3\ \text{particle}) = 8.01 \times 10^8\ \text{g mol}^{-1} - 100 \times 3574.66\ \text{g mol}^{-1}$

$M(\text{CaCO}_3\ \text{particle}) = 8.01 \times 10^8\ \text{g mol}^{-1}$

Mass of one $CaCO_3$ particle: $m(\text{CaCO}_3\ \text{particle}) = M(\text{CaCO}_3\ \text{particle}) \cdot N_A^{-1}$

and with the volume of the spherical particle ($V = \frac{4}{3}\pi r^3$) the density can be calculated:

$$\rho(\text{CaCO}_3) = \frac{m(\text{CaCO}_3\text{ particle})}{V(\text{CaCO}_3\text{ particle})} = \frac{3\,m(\text{CaCO}_3\text{ particle})}{4\pi r^3}$$

$$= \frac{3\,(M\ (\text{total particle}) - N_{\text{polymer}}\ M(\text{polymer})\ )}{N_a 4\pi\, r^3}$$

$$= \frac{3 \times 8.01 \times 10^8\ \text{g mol}^{-1}}{N_A \cdot 4\pi\,(5\times10^{-6}\text{cm})^3} = 2.54\ \text{g cm}^{-3}$$

The modification of calcium carbonate is Calcite ☐ Vaterite ☒ Aragonite ☐

PROBLEM 6

Alkalinity of Water and Solubility of CO_2

The capacity of water to accept H^+ ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO_3^-, CO_3^{2-}, and OH^-. At *pH* values below 7, H^+ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO_3^-, CO_3^{2-}, and OH^- are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$$

The contributions made by different species to alkalinity depend upon pH. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \quad K_{CO_2} = 3.44\times10^{-2}$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \qquad K_{H_2CO_3} = 2.00\times10^{-3}$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad K_{a1} = 2.23\times10^{-4}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad K_{a2} = 4.69\times10^{-11}$$

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad K_{sp} = 4.50\times10^{-9}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = 1.00\times10^{-14}$$

Note: Calculations must be shown.

6.1 Natural waters (river or lake water) generally contain dissolved CO_2. The ratio of $[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}]$ in a water at $[H^+] = 1.00\times10^{-7}$ M will be:

_(a)_ : 1.00 : _(b)_. Calculate (a) and (b).

6.2 Gaseous CO_2 in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of $CO_{2\,(aq)}$ (mol dm^{-3}) in pure water that is in equilibrium with the unpolluted air at 1.01×10^5 Pa and 298 K containing 0.0360 % (molar ratio) CO_2. (assuming standard pressure = 1.01×10^5 Pa).

If you are unable to solve this problem, assume that concentration of $CO_{2\ (aq)}$ is equal to 1.11×10^{-5} M for further calculations.

The solubility (S) of CO_2 in water can be defined as

S = $[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$.

The solubility of atmospheric CO_2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01×10^5 Pa will vary with alkalinity.

6-3 Find the solubility of atmospheric CO_2 in pure water (mol dm^{-3}). Neglect dissociation of water.

6.4 Find the solubility of atmospheric CO_2 (mol dm^{-3}) in a 1.00×10^{-3} mol dm^{-3} NaOH solution.

At 298 K, 1.01×10^5 Pa unpolluted air is in equilibrium with natural water saturated with $CaCO_3$. The following main equilibrium may exist:

$$CaCO_{3(s)} + CO_{2\ (aq)} + H_2O \rightleftharpoons Ca^{2+} + 2\ HCO_3^-$$

6.5 Calculate the equilibrium constant for the above equation.

If you are unable to solve this problem, assume that equilibrium constant $K_{eq} = 5.00\times10^{-5}$ for further calculations.

6.6 Calculate the concentration of Ca^{2+} (mg dm^{-3}) in $CaCO_3$-saturated natural water that is in equilibrium with atmospheric CO_2.

If you are unable to solve this problem, assume that concentration of $Ca^{2+}_{(aq)}$ = 40.1 mg dm^{-3} for further calculations.

6.7 Find the alkalinity (mol/L) of the above solution.

6.8 In an underground lake saturated with $CaCO_3$, the water has a high content of CO_2. The concentration of Ca^{2+} in this lake was found to be as high as 100 mg dm^{-3}. Assume the lake and the air above is a closed system, calculate the effective pressure of CO_2 (Pa) in air which is in equilibrium with this Ca^{2+} content.

SOLUTION

6.1 $[H^+] = 1.00\times10^{-7}$

$K_{a1} = [HCO_3^-]\,[H^+] / [H_2CO_3] = 2.23\times10^{-4}$,

$[HCO_3^-] / [H_2CO_3] = 2.23\times10^{3}$

$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69\times10^{-11}$,

$[CO_3^{2-}] / [HCO_3^-] = 4.69\times10^{-4}$

$[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] = \mathbf{4.48\times10^{-4}} : 1.00 : \mathbf{4.69\times10^{-4}}$

6.2 $p(CO_2(aq)) = 1.01\times10^{5}\text{ Pa}\times 3.60\times10^{-4} = 36.36\text{ Pa}$

$[CO_2(aq)] = K_{CO_2}\times p(CO_2) = 0.0344\times(36.36\text{ Pa} / 1.01\times10^{5}\text{ Pa}) = \mathbf{1.24\times10^{-5}}$

(If you are unable to solve this problem, for further calculations assume that $[CO_2(aq)] = 1.11\times10^{-5}$.)

6.3

(a) Solubility = $[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-]$

($[H_2CO_3] = [CO_2(aq)]\times K_{H_2CO_3} = 2.48\times10^{-8}$

and $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69\times10^{-11}$

both can be neglected.)

$[H^+][HCO_3^-] / [CO_2(aq)] = K_{a1}\ K_{H_2CO_3} = (2.23\times10^{-4})\ (2.00\times10^{-3}) = 4.46\times10^{-7}$

From 6-2: $[CO_2(aq)] = 1.24\times10^{-5}$,

$[H^+] = \mathbf{[HCO_3^-] = 2.35\times10^{-6}}$

Solubility = $[CO_2(aq)] + [HCO_3^-] = 1.24\times10^{-5} + 2.35\times10^{-6} = 1.48\times10^{-5}\text{ mol dm}^{-3}$

(b) (Using $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Solubility = $[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-]$

($[H_2CO_3] = [CO_2(aq)]\times \boldsymbol{K_{H_2CO_3}} = 2.22\times10^{-8}$ and $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69\times10^{-11}$ both can be neglected.)

$[H^+][HCO_3^-] / [CO_2(aq)] = K_{a1}\ K_{H_2CO_3} = (2.23\times10^{-4})\ (2.00\times10^{-3}) = 4.46\times10^{-7}$

From 6.2: $[CO_2(aq)] = 1.11\times10^{-5}$

$[H^+] = [\mathbf{HCO_3^-}] = 2.225\times10^{-6}$

Solubility = $[CO_2(aq)] + [HCO_3^-] = 1.11\times10^{-5} + 2.225\times10^{-6} = 1.34\times10^{-5}$

6.4 (Using $[CO_2(aq)] = 1.24\times10^{-5}$ for calculation)

In 1.00×10^{-3} mol dm^{-3} NaOH solution the solubility of CO_2 will be much higher because of the following reactions:

(1) $CO_2(aq) + 2\,OH^- \rightleftharpoons CO_3^{2-} + H_2O$ $\quad K = K_{H_2CO_3} \times K_{a1} \times K_{a2} / (1.00\times10^{-14})^2 = 2.09\times10^{11}$

(2) $CO_2(aq) + CO_3^{2-} + H_2O \rightleftharpoons 2\,HCO_3^-$ $\quad K = K_{H_2CO_3} \times K_{a1} / K_{a2} = 9.37\times10^{3}$

Combining (1) and (2): $CO_2(aq) + OH^- \rightleftharpoons HCO_3^-$ $\quad K = 4.43\times10^{7}$

With such a large K value all OH^- will finally be converted to HCO_3^-.

$$[HCO_3^-] = 1.00\times10^{-3}$$

$[OH^-] = 1.82\times10^{-6}$

$[H^+] = 5.49\times10^{-9}$ $\quad [CO_3^{2-}] = 8.54\times10^{-6}$

Solubility = $[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] =$

$= 1.24\times10^{-5} + 1.00\times10^{-3} + 8.54\times10^{-6} = 1.02\times10^{-3}$ mol dm^{-3}

6.5 $K_{eq} = K_{sp} \times K_{H_2CO_3} \times K_{a1} / K_{a2} = (4.50\times10^{-9}) \times (2.00\times10^{-3}) \times (2.23\times10^{-4}) / (4.69\times10^{-11}) =$

$= 4.28\times10^{-5}$

(If you are unable to solve this problem, assume that $K_{eq} = 5.00\times10^{-5}$ for further calculations.)

6.6

(a) (Using $K_{eq} = 4.28\times10^{-5}$ and $[CO_2(aq)] = 1.24\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-] / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.24\times10^{-5}$

$[Ca^{2+}] = 0.510\times10^{-3} = 20.5$ mg dm^{-3}

(b) (Using $K_{eq} = 5.00\times10^{-5}$ and $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.11\times10^{-5}$

$[Ca^{2+}] = 0.5177\times10^{-3}$ = 20.75 mg dm^{-3}

(c) (Using $K_{eq} = 5.00\times10^{-5}$ and $[CO_2(aq)] = 1.24\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.24\times10^{-5}$

$[Ca^{2+}] = 0.5372\times10^{-3}$ = 21.53 mg dm^{-3}

(d) (Using $K_{eq} = 4.28\times10^{-5}$ and $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.11\times10^{-5}$

$[Ca^{2+}] = 0.4916\times10^{-3}$ = 19.70 mg dm^{-3}

(If you are unable to solve this problem, assume that $[Ca^{2+}]_{(aq)}$ = 40.1 for further calculations.)

6.7 HCO_3^- is the major species in solution.

The *pH* of the solution can be estimated as $pH = (pK_{a1} + pK_{a2})/2 = (3.65 + 10.33) / 2 =$
$= 6.99 \approx 7.00$,

where K_{a1} and K_{a2} are the dissociation constants of H_2CO_3.

At pH 7.00, both $[OH^-]$ and $[H^+]$ can be neglected. Besides, $[CO_3^{2-}] << [HCO_3^-]$ (from **6.1**)

Alkalinity = $[HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \approx [HCO_3^-]$

From 6-6, mass balance, $[HCO_3^-] = 2\,[Ca^{2+}]$

(a) 1.02×10^{-3} (using $[Ca^{2+}]_{(aq)}$) from 6.6 (a))

(b) 1.035×10^{-3} (using $[Ca^{2+}]_{(aq)}$) from 6.6 (b))

(c) 1.0744×10^{-3} (using $[Ca^{2+}]_{(aq)}$ from 6-6 (c))

(d) 0.9831×10^{-3} (using $[Ca^{2+}]_{(aq)}$) from 6-6 (d))

(e) 2.00×10^{-3} (assuming $[Ca^{2+}]_{(aq)} = 40.1$)

Alkalinity = (a) or (b) or (c) or (d) or (e)

6.8

(a) (Using $K_{eq} = 4.28\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\,[Ca^{2+}]$

$[Ca^{2+}] = 100\text{ mg dm}^{-3} = 2.50\times10^{-3}\text{ mol dm}^{-3}$

Inserting into $K_{eq} = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = 4\,[Ca^{2+}] / [CO_2(aq)]$

$[CO_2(aq)] = 1.46\times10$

$p_{CO_2} = ([CO_2(aq)] / K_{CO_2}) \times 1.01\times10^5\text{ Pa} = 4.28\times10^3\text{ Pa}$

(b) (Using $K_{eq} = 5.00\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\,[Ca^{2+}]$

$[Ca^{2+}] = 100\text{ mg dm}^{-3} = 2.50\times10^{-3}\text{ mol dm}^{-3}$

Inserting into $K_{eq} = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = 4\,[Ca^{2+}] / [CO_2(aq)]$

$[CO_2(aq)] = 1.25\times10^{-3}$

$p_{CO_2} = ([CO_2(aq)] / K_{CO_2}) \times 1.01\times10^5\text{ Pa} = 3.67\times10^3\text{ Pa}$

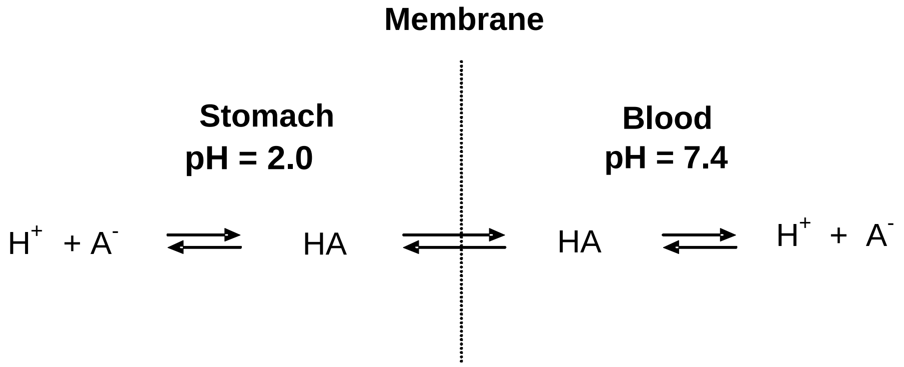
PROBLEM 5

Acid-Base Chemistry

5.1 Calculate [H^+], [OH^-], [HSO_4^-], and [SO_4^{2-}] in a 1.0×10^{-7} M solution of sulfuric acid ($K_w = 1.0\times10^{-14}$, $K_2 = 1.2\times10^{-2}$ at 25 °C). In your work you may use mass- and charge-balance equations. Answer with two significant figures.

5.2 Calculate the volume of 0.80 M NaOH solution that should be added to a 250 cm^3 aqueous solution containing 3.48 cm^3 of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. Answer with three significant figures. (H_3PO_4 (aq), purity = 85 mass %, density = 1.69 g/cm^3, M_r = 98.00) (pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.44).

5.3 The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. Calculate the ratio of the total concentration ([HA] + [A^-]) of aspirin (acetylsalicylic acid, pK = 3.52) in the blood to that in the stomach.

SOLUTION

5.1 1st ionization is complete: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$[H_2SO_4] = 0$

2nd ionization: $[H^+][SO_4^{2-}] / [HSO_4^-] = K_2 = 1.2\times10^{-2}$ (1)

Mass balance: $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}] = 1.0\times10^{-7}$ (2)

Charge balance: $[H^+] = [HSO_4^-] + 2 [SO_4^{2-}] + [OH^-]$ (3)

Degree of ionization is increased upon dilution.

$[H_2SO_4] = 0$

Assume $[H^+]_{H_2SO_4} = 2\times10^{-7}$

From (1): $[SO_4^{2-}] / [HSO_4^-] = 6\times10^4$ (2nd ionization is almost complete)

$[HSO_4^-] = 0$

From (2): $[SO_4^{2-}] = 1.0\times10^{-7}$

From (3): $[H^+] = (2\times10^{-7}) + 10^{-14} / [H^+]$

$[H^+] = 2.4\times10^{-7}$ (pH = 6.6)

$[OH^-] = 1\times10^{-14} / (2.4\times10^{-7}) = 4.1\times10^{-8}$

From (1):

$[HSO_4^-] = [H^+] [SO_4^{2-}] / K_2 = (2.4\times10^{-7}) \times (1.0\times10^{-7}) / (1.2\times10^{-2}) = 2.0\times10^{-12}$

Check charge balance:

$2.4\times10^{-7} \approx (2.0\times10^{-12}) + 2 (1.0\times10^{-7}) + (4.1\times10^{-8})$

Check mass balance:

$0 + 2.0\times10^{-12} + 1.0\times10^{-7} \approx 1.0\times10^{-7}$

5.2 $n(H_3PO_4) = 0.85 \times 3.48\ cm^3 \times 1.69\ g\ cm^{-3} \times 1\ mol / 98.00\ g \times 1000 = 51.0\ mmol$

The desired pH is above pK_2.

A 1:1 mixture of $H_2PO_4^-$ and HPO_4^{2-} would have $pH = pK_2 = 7.20$.

If the pH is to be 7.40, there must be more HPO_4^{2-} than $H_2PO_4^-$.

We need to add NaOH to convert H_3PO_4 to $H_2PO_4^-$ and to convert to the right amount of $H_2PO_4^-$ to HPO_4^{2-}.

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

The volume of 0.80 NaOH needed to react with to convert H_3PO_4 to $H_2PO_4^-$ is:

51.0 mmol / 0.80 mol dm^{-3} = 63.75 cm^3

To get *pH* of 7.40 we need:

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-}$$

	$H_2PO_4^-$	OH^-	HPO_4^{2-}
Initial mmol	51.0	x	0
Final mmol	51.0 – x	0	x

$pH = pK_2 + \log [HPO_4^{2-}] / [H_2PO_4^-]$

7.40 = 7.20 + log {x / (51.0 – x)}; x = 31.27 mmol

The volume of NaOH needed to convert 31.27 mmol is:

31.27 mmol / 0.80 mol dm^{-3} = 39.09 cm^3

The total volume of NaOH = 63.75 + 39.09 = 102.84 cm^3 ≈ 103 cm^3

5.3 $pK = 3.52$

$pH = pK_a + \log ([A^-] / [HA])$

$[A^-] / [HA] = 10^{(pH-pKa)}$

In blood, *pH* = 7.40, $[A^-] / [HA] = 10^{(7.40-3.52)} = 7586$

Total ASA = 7586 + 1 = 7587

In stomach, *pH* = 2.00, $[A^-] / [HA] = 10^{(2.00 - 3.52)} = 3.02\times10^{-2}$

Total ASA = 1 + 3.02×10^{-2} = 1.03

Ratio of total aspirin in blood to that in stomach = 7587 / 1.03 = 7400

PROBLEM 6

Electrochemistry

Water is a very stable molecule, abundant on earth and essential for life. As such, water was long thought to be a chemical element. However, soon after the invention of a voltaic cell in 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by electrolysis.

6.1 Water can be thought of as hydrogen oxidized by oxygen. Thus, hydrogen can be recovered by reduction of water, using an aqueous solution of sodium sulfate, at a platinum electrode connected to the negative terminal of a battery. The solution near the electrode becomes basic. Write a balanced half-reaction for the reduction of water.

6.2 Water can also be thought of as oxygen reduced by hydrogen. Thus, oxygen can be recovered by oxidation of water at the Pt electrode connected to the positive terminal. Write a balanced half-reaction for the oxidation of water.

6.3 When copper is used at both electrodes, gas is generated only at one electrode during the initial stage of electrolysis. Write the half-reaction at the electrode that does not generate gas.

Another species in solution that can be reduced is sodium ion. The reduction of sodium ion to metallic sodium does not occur in aqueous solution because water is reduced first. However, as Humphrey Davy discovered in 1807, sodium can be made by electrolysis of fused sodium chloride.

6.4 Based on these observations, connect the half-reactions with the standard reduction potential (in volts).

Reduction of copper ion (Cu^{2+})	+ 0.340
Reduction of oxygen	– 2.710
Reduction of water	– 0.830
Reduction of sodium ion (Na^{+})	0.000
Reduction of hydrogen ion	+1.230

The electrode potential is affected by other reactions taking place around the electrode. The potential of the Cu^{2+}/Cu electrode in a 0.100 M Cu^{2+} solution changes as $Cu(OH)_2$ precipitates. Answer with 3 significant figures for the following problems. The temperature is 25 °C. Note that $K_w = 1.00 \times 10^{-14}$ at 25 °C.

6.5 Precipitation of $Cu(OH)_2$ begins at pH = 4.84. Determine the solubility product of $Cu(OH)_2$.

6.6 Calculate the standard reduction potential for $Cu(OH)_2(s) + 2\,e^- \rightarrow Cu(s) + 2\,OH^-$.

6.7 Calculate the electrode potential at *pH* = 1.00.

Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge recharge cycles, the following reversible half-reactions occur.

$LiCoO_2 \rightleftarrows Li_{1-x}\,CoO_2 + x\,Li^+ + x\,e^-$

$C + x\,Li^+ + x\,e^- \rightleftarrows CLi_x$

The total amount of energy a battery can store, is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

6.8 Graphite has lithium intercalation sites between its layers. Assuming a maximum 6 : 1 carbon-to-lithium intercalation stoichiometry, calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g with 3 significant figures.

SOLUTION

6.1 $4\,H_2O + 4\,e^- \rightarrow 2\,H_2(g) + 4\,OH^-$ (or $2\,H_2O + 2\,e^- \rightarrow H_2(g) + 2\,OH^-$)

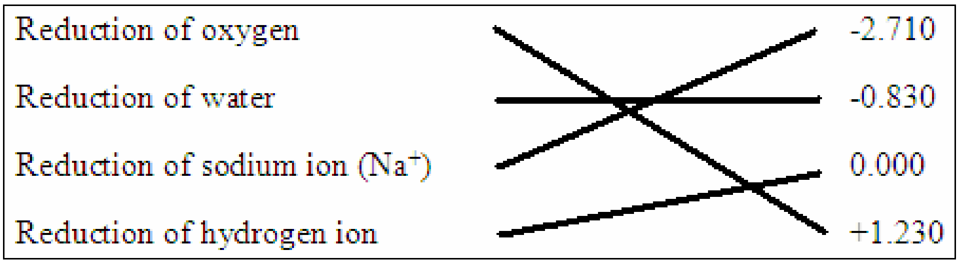
6.2 $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$ (or $H_2O \rightarrow 1/2\,O_2 + 2\,H^+ + 2\,e^-$)

6.3 $Cu \rightarrow Cu^{2+} + 2e^-$

6.4 Reduction of sodium ion seldom takes place.

It has a highly negative reduction potential of –2.710 V.

Reduction potential for water to hydrogen is negative (water is very stable).
But, it is not as negative as that for sodium ion. It is –0.830 V.
Reduction of both copper ion and oxygen takes place readily and the reduction potentials for both are positive.
In the present system, the reverse reaction (oxidation) takes place at the positive terminal. Copper is oxidized before water.
Reduction potential for hydrogen ion is defined as 0.000 V.



6.5 $pOH = 14.00 – 4.84 = 9.16$

$[OH^-] = 6.92\times10^{-10}$

$K_{sp} = [Cu^{2+}]\,[OH^-]^2 = 0.100 \times (6.92\times10^{-10}) = 4.79\times10^{-20}$

6.6 $E = E^o(Cu^{2+}/\,Cu) + (0.0592\,/\,2) \log [Cu^{2+}] = +0.340 + (0.0592/2) \log [Cu^{2+}] =$

$= +0.340 + (0.0592\,/\,2) \log (K_{sp}\,/\,[OH^-]^2)$

$= +0.340 + (0.0592\,/\,2) \log K_{sp} - (0.0592\,/\,2) \log [OH^-]^2$

$= +0.340 + (0.0592\,/\,2) \log K_{sp} - 0.0592 \log [OH^-]$,

By definition, the standard potential for

$Cu(OH)_2(s) + 2\,e^- \rightarrow Cu(s) + 2\,OH^-$

is the potential where $[OH^-] = 1.00$.

$E = E^o\left(Cu(OH)_2\,/\,Cu\right) = +\,0.340 + (0.0592/2) \log K_{sp}$

$= +\,0.340 + (0.0592\,/\,2) \log (4.79\times10^{-20})$

$= +\,0.340 – 0.572$

$= –\,0.232$ V

One may solve this problem as follows.

Eqn 1: $Cu(OH)_2(s) + 2\ e^- \rightarrow Cu + 2\ OH^-$

$E_+^o = E^o\big(Cu(OH)_2 / Cu) = ?$

Eqn 2: $Cu(OH)_2(s) \rightarrow Cu^{2+} + 2\ OH^-$

$E^o = (0.05916 / n) \log K_{sp} = (0.05916 / 2) \log(4.79\times10^{-20}) = -0.5715$ V

Eqn 1 – Eqn 2 : $Cu^{2+} + 2\ e^- \rightarrow Cu$

$E_-^o = E_+^o - E^o = E^o\,(Cu^{2+} / Cu) = 0.34$ V

Therefore, $E_+^o = E_-^o + E^o = +\ 0.34 + (-0.5715)\ = \ = -0.232$ V

6.7 Below *pH* = 4.84, there is no effect of $Cu(OH)_2$ because of no precipitation. Therefore,

$E = E\,(Cu^{2+} / Cu) = +0.340 + (0.0592 / 2) \log [Cu^{2+}] =$

$= +0.340 + (0.0592 / 2) \log 0.100 = +0.340 - 0.0296 = +0.310$ V

6.8 1.00 g graphite = 0.0833 mol carbon

6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.

Therefore, 1 g graphite can charge 96487 × 0.0139 = 1340 coulombs.

1340 coulombs / g = 1340 A sec / g = 1340 × 1000 mA × (1 / 3600) h =

= 372 mAh / g

PROBLEM 4

Determination of water by Fischer titraton

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO_2 and pyridine (C_5H_5N, Py) – Fischer reagent. The following reactions occur during the titration:

$SO_2 + CH_3OH + H_2O + I_2 \rightarrow 2\ HI + CH_3OSO_3H$

$Py + HI \rightarrow PyH^+I^-$

$Py + CH_3OSO_3H \rightarrow PyH^+CH_3OSO_3^-$

Iodine content is usually expressed in mg of water reacting with 1 cm^3 of the titrant solution (hereunder T, mg cm^{-3}), which equals the mass of water (mg) reacting with 1.00 cm^3 of the iodine solution. T is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I_2 with SO_2 and H_2O occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:

4.2 12.20 cm^3 of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate $Na_2C_4H_4O_6 \cdot 2\ H_2O$.

4.3 A known amount of water (21.537 g) was placed into a 1.000 dm^3 volumetric flask which was filled by methanol up to the mark. For titration of 10.00 cm^3 of the obtained solution, 22.70 cm^3 of Fischer reagent solution were needed, whereas 2.20 cm^3 of iodine were used for titration of 25.00 cm^3 of methanol.

4.4 5.624 g of water were diluted by methanol up to a total volume of 1.000 dm^3 (solution **A**); 22.45 cm^3 of this solution were used for titration of 15.00 cm^3 of a Fischer reagent (solution **B**).

Then 25.00 cm^3 of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 cm^3 of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 cm^3 of the latter solution were spent.

4.5 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound $Fe_2(SO_4)_3 \cdot x\, H_2O$, 10.59 cm^3 of iodine solution (T = 15.46 mg/ cm^3) were consumed.

4.6 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.

4.7 Write down an equation of the overall reaction of $Fe_2(SO_4)_3 \cdot x\, H_2O$ with the Fischer reagent.

4.8 Calculate the composition of the hydrate $Fe_2(SO_4)_3 \cdot x\, H_2O$ (x = integer).

SOLUTION

4.1 Equation:

$$I_2 + SO_2 + 2\, H_2O + 4\, Py \rightarrow 2\, PyHI + (PyH)_2SO_4$$

4.2 T is equal to:

$M(Na_2C_4H_4O_6 \cdot 2\, H_2O) = 230.05\ g\ mol^{-1}$ $\quad 2 \times M(H_2O) = 36.04\ g\ mol^{-1}$

$$m(H_2O) = \frac{1.3520 \times 36.04}{230.05} = 0.2118\ g = 211.8\ mg$$

$$T = \frac{211.8}{12.20} = 17.36\ mg\ cm^{-3}$$

T = 17.36 mg cm^{-3}

4.3 T is equal to:

Volume of iodine consumed for 10 cm^3 of pure CH_3OH = $\frac{2.20 \times 10.00}{25.00} = 0.88\ cm^3$

$$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.88} = 9.87\ mg\ cm^{-3}$$

More exactly

10.00 cm^3 of the solution contains $\dfrac{(1000 - 21.5) \times 10.00}{1000}$ = 9.785 cm^3 of methanol.

Volume of iodine consumed for 9,785 cm^3 of pure CH_3OH = $\dfrac{2.20 \times 9{,}785}{25.00}$ =

= 0.86 cm^3

$$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.86} = 9.86 \text{ mg cm}^{-3}$$

T = 9.87 mg cm^{-3}

4.4 T is equal to:

Approach 1

Let 1 cm^3 of CH_3OH contains x mg H_2O, then 1 cm^3 of **A** contains

[(1.000 – 0.006) x + 5.624] mg H_2O.

15.00 T = 22.45 (0.994 x + 5.624) – 1st titration,

10.00 T = 25.00 x + 10.79 (0.994 x + 5.624) – 2nd titration.

Hence, x = 1.13 mg cm^{-3}, T = 10.09 mg cm^{-3} (10.10 without taking into account 0.994 factor)

Approach 2

Let y cm^3 of **B** be consumed for the titration of water, contained in 1 cm^3 of CH_3OH.

Then $T = \dfrac{22.45 \times 5.624}{15.00 - 22.45 \times 0.994 \times y}$ (1st titration) = $\dfrac{10.79 \times 5.624}{10.00 - 25.00\,y - 10.79\,y}$

(2nd titration).

Hence, y = 0.1116 and T = 10.10 mg cm^{-3}

T = 10.09 mg cm^{-3} (10.10 without taking into account 0.994 factor)

4.5 Equation(s):

$CaO + SO_2 \rightarrow CaSO_3$

$2\,CaO + 2\,I_2 \rightarrow CaI_2 + Ca(OI)_2$

$6\,CaO + 6\,I_2 \rightarrow 5\,CaI_2 + Ca(IO_3)_2$

(Instead of CaO, $Ca(OH)_2$ may be written.)

4.6 Equation(s):

$Fe_2(SO_4)_3 + 2\,HI \rightarrow 2\,FeSO_4 + \mathbf{I_2} + H_2SO_4$

$Fe_2(SO_4)_3$ + $\mathbf{H_2O}$ + SO_2 + CH_3OH → 2 $FeSO_4$ + CH_3OHSO_3 + H_2SO_4

(or in ionic form)

4.7 Equation:

$$Fe_2(SO_4)_3 \cdot x\,H_2O + (x-1)\,I_2 + x\,SO_2 + x\,CH_3OH \rightarrow 2\,FeSO_4 + x\,CH_3OHSO_3 + H_2SO_4 + 2(x-1)\,HI$$

4.8 The composition of the crystallohydrate is:

$M(Fe_2(SO_4)_3 \cdot x\,H_2O) = 399.9 + 18.02\,x$

$$m(H_2O) = \frac{0.6387 \times 18.02\,x}{(399.9 + 18.02\,x)}$$

$$m(H_2O) = 10.59\ \text{cm}^3 \times 15.46\ \text{mg cm}^{-3} \times 0.001\ \text{g mg}^{-1} \times \frac{x}{x-1}$$

$0.1637 \times (399.9 + 18.02\,x) = 11.51\,x - 11.51$

$x = 8.994 \approx 9$

Formula: $Fe_2(SO_4)_3 \cdot 9\,H_2O$

THE FORTIETH
INTERNATIONAL CHEMISTRY OLYMPIAD
12–21 JULY 2008, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A *pH* meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

1.1 Give the formulae of four acids that could have been in the solution if the *pH* changed one unit after a tenfold dilution.

1.2 Could it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: $pK_{a2} = 1.99$

☐ Yes ☐ No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.3 Could it be possible that the solution contained acetic acid?

Acetic acid: $pK_a = 4.76$

☐ Yes ☐ No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.4 Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.

EDTA: $pK_{a1} = 1.70$, $pK_{a2} = 2.60$, $pK_{a3} = 6.30$, $pK_{a4} = 10.60$

☐ Yes ☐ No

If yes, calculate the concentration.

SOLUTION

1.1 Any univalent, strong acid (HCl, HBr, HI, HNO_3, $HClO_4$) is acceptable. HF is not!

1.2 ☐ Yes ☑ No

No, the first dissociation step can be regarded as complete in aqueous solutions, thus $[H^+] > c_{acid.}$

No text or calculations are needed.

1.3 ☑ Yes ☐ No

Yes, but it can happen only in quite dilute solutions.

$c = [HA] + [A^–] = [H^+]$

$[H^+] = [A^–] + [OH^–]$

This means that $[HA] = [OH^–]$

$$K = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]([H^+] - [OH^-])}{[OH^-]} = \frac{[H^+]^3}{K_w} - [H^+]$$

The *pH* of the solution must be acidic, but close to 7.

6.5 is a good guess.

A good approximation is: $[H^+] = \sqrt[3]{(K\,K_w)}$

The full equation can be solved through iteration: $[H^+] = \sqrt[3]{(K + [H^+])K_w}$

Starting with a neutral solution two cycles of iteration give identical results:

$5.64 \times 10^{–7}$ mol dm^{-3} as the required concentration. Exact *pH* is 6.25.

1.4 ☑ Yes ☐ No

We can suppose that this solution would be quite acidic, so the 3rd and 4th dissociation steps can be disregarded. The following equations are thus true:

$c = [H_4A] + [H_3A^–] + [H_2A^{2–}] = [H^+]$

$[H^+] = [H_3A^–] + 2\,[H_2A^{2–}]$

This means that $[H_4A] = [H_2A^{2–}]$

$$K_1\,K_2 = \frac{[H^+]^2[H_2A^{2-}]}{[H_4A]} = [H^+]^2$$ (or $pH = (pK_1 + pK_2\,) / 2 = 2.15$)

$c = 0.0071$ mol dm^{-3}

PROBLEM 3

The chemical oxygen demand (COD) refers to the amount of oxidizable substance, such as organic compounds, in a sample solution, and it is used as an indication of water quality in seas, lakes, and marshes. For example, the COD of service water is kept below 1 mg dm^{-3}. The COD (mg dm^{-3}) is represented by mass of O_2 (mg) which accepts the same amount of electrons which would be accepted by the strong oxidizing agent when 1 dm^3 of a sample solution is treated with it. An example of the operation is presented below.

Analytical Operation

A sample solution with a volume of 1.00 dm^3 was acidified with a sufficient amount of sulphuric acid, and chloride ions were removed by the addition of silver nitrate solution. A volume of $1.00 \cdot 10^{-1}$ dm^3 of potassium permanganate solution ($c = 5.00 \cdot 10^{-3}$ mol dm^{-3}) was added to the sample solution, and the mixture was heated for 30 min. Further, a volume of $1.00 \cdot 10^{-1}$ dm^3 of disodium oxalate ($Na_2C_2O_4$ or NaOOC–COONa) standard solution ($c = 1.25 \cdot 10^{-2}$ mol dm^{-3}) was added, and the mixture was stirred well. Oxalate ions that remained unreacted were titrated with potassium permanganate solution ($c = 5.00 \cdot 10^{-3}$ mol dm^{-3}). A volume of $3.00 \cdot 10^{-2}$ dm^3 of the solution was used for the titration.

3.1 Give the equation of the redox reaction of potassium permanganate and disodium oxalate.

3.2 Calculate the mass of O_2 (in mg) that will oxidize the same number of moles of oxidizable substance as $1.00 \cdot 10^{-3}$ dm^3 of potassium permanganate solution with a concentration of $5.00 \cdot 10^{-3}$ mol dm^{-3} does.

3.3 From the following choices, select the most appropriate reason for the removal of chloride ions:

[A] Some of the chloride ions react with potassium permanganate, resulting in an error in COD.

[B] Some of the chloride ions react with disodium oxalate, resulting in an error in COD.

[C] Some of the chloride ions react with organic compounds in the sample solution, resulting in an error in COD.

[D] A colour is developed during titration, resulting in an error in COD.

3.4 Calculate the COD (mg dm^{-3}) of the sample solution described in the analytical operation above.

SOLUTION

3.1 $2\ KMnO_4 + 5\ Na_2C_2O_4 + 8\ H_2SO_4 \rightarrow 2\ MnSO_4 + 5\ Na_2SO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$

or

$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$

or

$2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$

3.2 The reactions of potassium permanganate and O_2 are as follows:

$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

$n(MnO_4^-) = 1.00 \cdot 10^{-3}\ dm^3 \times 5.00 \cdot 10^{-3}\ mol\ dm^{-3} = 5.00 \cdot 10^{-6}\ mol$

$n(O_2) = 5.00 \cdot 10^{-6}\ mol \times 5/4 = 6.25 \cdot 10^{-6}\ mol$

$m(O_2) = 6.25 \cdot 10^{-6}\ mol \times 32\ g\ mol^{-1} = 2.00 \cdot 10^{-4}\ g = 2.00 \cdot 10^{-1}\ mg$

3.3 The correct answer is [A].

3.4 The amounts of electrons used for reduction or oxidation are equal. Then:

$5 \times 5.00 \cdot 10^{-3}\ mol\ dm^{-3} \times (1.00 \cdot 10^{-1} + A)\ dm^3 =$

$= 2 \times 1.25 \cdot 10^{-2}\ mol\ dm^{-3} \times 1.00 \cdot 10^{-1}\ dm^3 + X \qquad (1)$

where A (cm^3) is an amount of potassium permanganate used for the final titration, and X (mol) is the amount of electrons for the oxidizable substance.

Equation (1) gives $X = 2.50 \cdot 10^{-2} \times A$.

When $A = 3.00 \cdot 10^{-2}\ dm^3$, $X = 7.50 \cdot 10^{-4}$ mol.

Hence, $COD = (32/4)\ g\ mol^{-1} \times 7.50 \cdot 10^{-4}\ mol \times 10^3\ (mg/g) \times 1/1\ (dm^{-3}) =$

$= 6.00\ mg\ dm^{-3}$

or

The amount of potassium permanganate consumed by the oxidizable substance, B (cm^3), is

$5 \times 5.00 \cdot 10^{-3} \times (1.00 \cdot 10^{-1} + A - B) = 2 \times 1.25 \cdot 10^{-2} \times 1.00 \cdot 10^{-1}$

At $A = 3.00 \cdot 10^{-2}\ dm^3$ B equals to $3.00 \cdot 10^{-2}\ dm^3$.

From the solution to question 3.2 above

$$\text{COD} = \frac{2.00\cdot 10^{-1}}{1.00\cdot 10^{-3}}\ (\text{mg dm}^{-3}) \times 3.00\cdot 10^{-2}\ (\text{dm}^{3}) \times 1/1\ (\text{dm}^{-3}) = 6.00\ \text{mg dm}^{-3}$$

PROBLEM 2

Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel. It produces no greenhouse gases on combustion.

In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the equation given below.

$$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(l)$$

The initial and final states are at 298 K. After combustion with 14.40 g of O_2, some of NH_3 remains unreacted.

2.1 Calculate the heat released during the process.

$\Delta_f H^o(NH_3(g)) = -46.11$ kJ mol^{-1} and $\Delta_f H^o(H_2O(l)) = -285.83$ kJ mol^{-1}

To determine the amount of NH_3 gas dissolved in water, produced during the combustion process, a 10.00 cm^3 sample of the aqueous solution was withdrawn from the reaction vessel and added to 15.0 cm^3 of a H_2SO_4 solution (c = 0.0100 mol dm^{-3}). The resulting solution was titrated with a standard NaOH solution (c = 0.0200 mol dm^{-3}) and the equivalence point was reached at 10.64 cm^3.

($K_b(NH_3) = 1.8 \cdot 10^{-5}$; $K_a(HSO_4^-) = 1.1 \cdot 10^{-2}$)

2.2 Calculate pH of the solution in the container after combustion.

2.3 At the end point of titration, NH_4^+ and SO_4^{2-} ions are present in the solution. Write the equations for the relevant equilibria to show how the presence of these two ions affects the pH and calculate their equilibrium constant(s).

2.4 Tick the correct statement for the pH of the solution at the equivalence point.

☐ pH > 7 ☐ pH = 7 ☐ pH < 7

SOLUTION

2.1 $q_v = \Delta E = \Delta H - \Delta n_g RT$

For 1 mole of NH_3:

$\Delta H = 3/2 \times (-285.83) - (-46.11) = -382.64$ kJ

$\Delta n_g = -1.25$ mol

$\Delta E = -382.64\text{ kJ} - [(-1.25\text{ mol}) \times 8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 298\text{ K}] = -379.5\text{ kJ}$

$$n(O_2) = \frac{14.4\text{ g}}{32.0\text{ g mol}^{-1}} = 0.450\text{ mol}$$

$n(NH_3)_{\text{reacted}} = 0.450\text{ mol} \times 4/3 = 0.600\text{ mol}$

$q_v = \Delta E = 0.600\text{ mol} \times (-379.5\text{ kJ mol}^{-1}) = \underline{-227.7\text{ kJ}}$

2.2 Total $n(H_2SO_4) = 15.00\text{ cm}^3 \times 0.0100\text{ mol dm}^{-3} = 0.150\text{ mmol}$

$H_2SO_4 + 2\text{ NaOH} \rightarrow Na_2SO_4 + 2\text{ }H_2O$

After back titration with NaOH:

$n(H_2SO_4)_{\text{reacted}} = ½\ n(\text{NaOH})_{\text{reacted}} = ½\ (0.01064\text{ dm}^3 \times 0.0200\text{ mol dm}^{-3}) =$

$= 1.064 \cdot 10^{-4}\text{ mol} = 0.1064\text{ mmol}$

$n(H_2SO_4)_{\text{reacted with }NH_3} = 0.0436\text{ mmol}$

$2\text{ }NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$n(NH_3) = 2 \times n(H_2SO_4)_{\text{reacted with }NH_3} = 2 \times 0.0436\text{ mmol} = 0.0872\text{ mmol}$

$$c(NH_3) = \frac{0.0872\text{ mmol}}{0.0100\text{ dm}^3} = 8.72 \cdot 10^{-3}\text{ mol dm}^{-3}$$

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

$c - x$ x x

$$K_b = 1.8 \cdot 10^{-5} = \frac{x^2}{0.00872 - x}$$

$x = [OH^-] = 3.96 \cdot 10^{-4}$

$pOH = 3.41$

$pH = 10.59$

2.3 $SO_4^{2-}(aq) + H_2O(l) \rightleftarrows HSO_4^-(aq) + OH^-(aq)$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \cdot 10^{-14}}{1.1 \cdot 10^{-2}} = 9.1 \cdot 10^{-13}$$

$NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq)$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} = 5.6 \cdot 10^{-10}$$

2.4 The correct answer: $pH < 7.0$

PROBLEM 6

Extraction of gold using sodium cyanide, a very poisonous chemical, causes environmental problems and gives rise to serious public concern about the use of this so called "cyanide process". Thiosulfate leaching of gold has been considered as an alternative. In this process, the main reagent is ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is relatively non-toxic. Although this process appears to be environmentally benign, the chemistry involved is very complex and needs to be studied thoroughly. The solution used for leaching gold contains $S_2O_3^{2-}$, Cu^{2+}, NH_3, and dissolved O_2. The solution must have a pH greater than 8.5 to allow free ammonia to be present.

According to the proposed mechanism, a local voltaic micro-cell is formed on the surface of gold particles during the leaching process and operates as follows:

Anode:

$Au(s) + 2\ NH_3(aq) \longrightarrow [Au(NH_3)_2]^+(aq) + e^-$

$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

Cathode:

$[Cu(NH_3)_4]^{2+}(aq) + e^- \longrightarrow [Cu(NH_3)_2]^+(aq) + 2\ NH_3(aq)$

$[Cu(NH_3)_2]^+(aq) + 3\ S_2O_3^{2-}(aq) \longrightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 2\ NH_3(aq)$

6.1 Write the overall cell reaction for this voltaic cell.

6.2 In the presence of ammonia $[Cu(S_2O_3)_3]^{5-}$ is oxidized by O_2 back to $[Cu(NH_3)_4]^{2+}$. Write a balanced equation for this oxidation-reduction reaction in basic solution.

6.3 In this leaching process, the $[Cu(NH_3)_4]^{2+}$ complex ion functions as catalyst and speeds up the dissolution of gold. Write the net overall oxidation-reduction reaction for dissolution of the gold metal, which is catalyzed by $[Cu(NH_3)_4]^{2+}$ complex ion.

6.4 Draw the coordination geometries of the metal in $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complex ions, indicating the coordinating atoms.

The formation constants, K_f, of $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complexes are $1.00 \cdot 10^{26}$ and $1.00 \cdot 10^{28}$, respectively. Consider a leaching solution in which the equilibrium concentrations of the species are as follows:

$[S_2O_3^{2-}] = 0.100$; $[NH_3] = 0.100$ and the total concentration of gold(I) species = $5.50 \cdot 10^{-5}$ mol dm^{-3}.

6.5 Calculate the percentage of gold(I) ion that exists in the form of thiosulfate complex.

When the concentration of O_2 is not high enough and pH > 10, $S_2O_3^{2-}$ reduces $[Cu(NH_3)_4]^{2+}$ to $[Cu(S_2O_3)_3]^{5-}$ with the formation of tetrathionate ion $S_4O_6^{2-}$:

$$2\,[Cu(NH_3)_4]^{2+}(aq) + 8\,S_2O_3^{2-}\,(aq) \rightarrow 2\,[Cu(S_2O_3)_3]^{5-}\,(aq) + S_4O_6^{2-}\,(aq) + 8\,NH_3(aq)$$

In basic solution tetrathionate disproportionates to trithionate, $S_3O_6^{2-}$, and thiosulfate.

6.6 Write a balanced equation for this disproportionation reaction.

6.7 When the O_2 concentration is too high, $S_2O_3^{2-}$ is oxidized by oxygen to yield trithionate and sulfate ions. Write a balanced equation for this reaction.

SOLUTION

6.1 Net anode half reaction:

$Au(s) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + e^-$

Net cathode half reaction:

$[Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^- \rightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq)$

erall cell reaction:

$Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq)$
$+ 4\ NH_3(aq)$

6.2 Oxidation half reaction:

$[Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^-$

Reduction half reaction:

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-\ (aq)$

Redox reaction:

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \rightarrow$
$\rightarrow 4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)$

6.3 $Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq) +$
$+ 4\ NH_3(aq)$

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \rightarrow$
$\rightarrow 4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)$

Summarizing the above equations:

$4\ Au(s) + 8\ S_2O_3^{2-}(aq) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ [Au(S_2O_3)_2]^{3-}(aq) + 4\ OH^-(aq)$

6.4	$[Au(NH_3)_2]^+$	$[Au(S_2O_3)_2]^{3-}$
Coordination geometry:	$[H_3N\text{-}Au\text{-}NH_3]^+$	$[O_3S\text{-}S\text{-}Au\text{-}S\text{-}SO_3]^{3-}$

6.5 $Au^+(aq) + 2\ NH_3(aq) \rightarrow [Au(NH_3)_2]^+(aq)$ $K_{f,1} = 1.00\ .\ 10^{26}$

$Au^+(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq)$ $K_{f,2} = 1.00\ .\ 10^{28}$

$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

$$K_{eq} = \frac{K_{f,2}}{K_{f,1}} = 1.00 \cdot 10^2$$

$[Au(NH_3)_2]^+ + [Au(S_2O_3)_2]^{3-} = 5.50 \cdot 10^{-5}$ mol dm^{-3}

$$K_{eq} = \frac{(0.100)^2\ x}{(5.50 \cdot 10^{-5} - x)\ (0.100)^2} = 1.00 \cdot 10^2$$

$x = 5.445 \cdot 10^{-5}$

$$\frac{5.445 \cdot 10^{-5}}{5.50 \cdot 10^{-5}} \times 100 = 99.0\ \%$$

Thus, 99.0 % of Au(I) is in the form of $[Au(S_2O_3)_2]^{3-}$.

6.6 $S_4O_6^{2-}(aq) + 2\ e^- \rightarrow 2\ S_2O_3^{2-}(aq)$

$12\ OH^-(aq) + 3\ S_4O_6^{2-}(aq) \rightarrow 4\ S_3O_6^{2-}(aq) + 6\ H_2O(l) + 10\ e^-$

$4\ S_4O_6^{2-}(aq) + 6\ OH^-(aq) \rightarrow 5\ S_2O_3^{2-}(aq) + 2\ S_3O_6^{2-}(aq) + 3\ H_2O(l)$

disproportionation

6.7 $2\ S_2O_3^{2-}(aq) + 2\ O_2(g) \rightarrow SO_4^{2-}(aq) + S_3O_6^{2-}(aq)$

PROBLEM 3

Thiomolybdate ions are derived from molybdate ions, MoO_4^{2-}, by replacing oxygen atoms with sulfur atoms. In nature, thiomolybdate ions are found in such places as the deep waters of the Black Sea, where biological sulfate reduction generates H_2S. The molybdate to thiomolybdate transformation leads to rapid loss of dissolved Mo from seawater to underlying sediments, depleting the ocean in Mo, a trace element essential for life.

The following equilibria control the relative concentrations of molybdate and thiomolybdate ions in dilute aqueous solution:

$MoS_4^{2-} + H_2O(l) \rightleftharpoons MoOS_3^{2-} + H_2S(aq)$ $K_1 = 1.3 \cdot 10^{-5}$

$MoOS_3^{2-} + H_2O(l) \rightleftharpoons MoO_2S_2^{2-} + H_2S(aq)$ $K_2 = 1.0 \cdot 10^{-5}$

$MoO_2S_2^{2-} + H_2O(l) \rightleftharpoons MoO_3S^{2-} + H_2S(aq)$ $K_3 = 1.6 \cdot 10^{-5}$

$MoO_3S^{2-} + H_2O(l) \rightleftharpoons MoO_4^{2-} + H_2S(aq)$ $K_4 = 6.5 \cdot 10^{-6}$

3.1 If at equilibrium the concentrations of MoO_4^{2-} and $H_2S(aq)$ are equal to $1{\cdot}10^{-7}$ and $1{\cdot}10^{-6}$, respectively, what would be the equilibrium concentration of MoS_4^{2-}?

Solutions containing $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-} display absorption peaks in the visible wavelength range at 395 and 468 nm. The other ions, as well as H_2S, absorb negligibly in the visible wavelength range. The molar absorptivities (ε) at these two wavelengths are given in the following table:

	ε at 468 nm $dm^3\ mol^{-1}\ cm^{-1}$	ε at 395 nm $dm^3\ mol^{-1}\ cm^{-1}$
MoS_4^{2-}	11870	120
$MoOS_3^{2-}$	0	9030
$MoO_2S_2^{2-}$	0	3230

3.2 A solution *not* at equilibrium contains a mixture of MoS_4^{2-}, $MoOS_3^{2-}$ and $MoO_2S_2^{2-}$ and no other Mo-containing species. The total concentration of all species containing Mo is $6.0 \cdot 10^{-6}$ mol dm^{-3}. In a 10.0 cm absorption cell, the absorbance of the solution at 468 nm is 0.365 and that at 395 nm is 0.213. Calculate the concentrations of all three Mo-containing anions in this mixture.

A solution with initial concentration of MoS_4^{2-} equal to $2.0 \cdot 10^{-7}$ mol dm^{-3} hydrolyzes in a closed system. The H_2S product accumulates until equilibrium is reached. When calculating the final equilibrium concentrations of H_2S(aq), and all five Mo-containing anions (that is, MoO_4^{2-}, $MoOS_3^{2-}$, $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-}) ignore the possibility that H_2S might ionize to HS^- under certain pH conditions.

3.3 Write the six independent equations that determine the system.

3.4 Calculate the above mentioned six concentrations making reasonable approximations, giving your answers to two significant figures.

SOLUTION

3.1 Multiplying the mass action laws for the four given reactions produces:

$$\frac{[MoO_4^{2-}]\,[H_2S]^4}{[MoS_4^{2-}]} = \frac{1\cdot 10^{-7}\,(1\cdot 10^{-6})^4}{[MoS_4^{2-}]} = 1.4\cdot 10^{-20}$$

$$[MoS_4^{2-}] = 7\cdot 10^{-12}$$

3.2 MoS_4^{2-} concentration is determined by absorbance at 468 nm:

$0.365 = 11870 \times 10.0 \times c(MoS_4^{2-})$

$c(MoS_4^{2-}) = 3.08\cdot 10^{-6}$ mol dm^{-3}

From conservation of Mo:

$c(MoOS_3^{2-}) + c(MoO_2S_2^{2-}) = c(Mo)_{Total} - c(MoS_4^{2-}) =$

$= (6.0\cdot 10^{-6} - 3.08\cdot 10^{-6})$ mol dm^{-3} $= 2.9\cdot 10^{-6}$ mol dm^{-3}

By rearrangement:

$c(MoO_2S_2^{2-}) = 2.9\cdot 10^{-6}$ mol dm^{-3} $- c(MoOS_3^{2-})$

From optical absorbance at 395 nm (quantities in the equations are without dimensions):

$0.213 = (120 \times 10.0 \times 3.08\cdot 10^{-6}) + (9030 \times 10.0 \times c(MoOS_3^{2-})) +$

$+ (3230 \times 10.0 \times c(MoO_2S_2^{2-}))$

$0.213 = (120 \times 10.0 \times 3.08\cdot 10^{-6}) + (9030 \times 10.0 \times c(MoOS_3^{2-})) +$

$+ (3230)(10.0)(2.9\cdot 10^{-6} - c(MoOS_3^{2-}))$

$c(MoOS_3^{2-}) = 2.0\cdot 10^{-6}$ mol dm^{-3}

$c(MoO_2S_2^{2-}) = 2.9\cdot 10^{-6} - c(MoOS_3^{2-}) = 0.9\cdot 10^{-6}$ mol dm^{-3}

3.3 Mass balance for Mo:

$2.0\cdot 10^{-7} = c(MoS_4^{2-}) + c(MoOS_3^{2-}) + c(MoO_2S_2^{2-}) + c(MoO_3S^{2-}) + c(MoO_4^{2-})$ (1)

Mass balance for S:

$8.0\cdot 10^{-7} = 4\,c(MoS_4^{2-}) + 3\,c(MoOS_3^{2-}) + 2\,c(MoO_2S_2^{2-}) + c(MoO_3S^{2-}) + (H_2S)$ (2)

Equilibrium constants:

$$1.3\cdot10^{-5}=\frac{[\mathrm{MoOS_3^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoS_4^{2-}}]} \qquad (3)$$

$$1.0\cdot10^{-5}=\frac{[\mathrm{MoO_2S_2}^{2-}][\mathrm{H_2S}]}{[\mathrm{MoOS_3^{2-}}]} \qquad (4)$$

$$1.6\cdot10^{-5}=\frac{[\mathrm{MoO_3S^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoO_2S_2^{2-}}]} \qquad (5)$$

$$6.5\cdot10^{-6}=\frac{[\mathrm{MoO_4^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoO_3S^{2-}}]} \qquad (6)$$

3.4 It is likely that multiple approaches will be found for solving these equations. Here is one approach:

The maximum possible H_2S concentration is $8.0\cdot10^{-7}$ mol dm^{-3} if complete hydrolysis occurs. At this H_2S concentration, MoO_3S^{2-} is only about 12 % of $c(\mathrm{MoO_4^{2-}})$ and the remaining thio anions are much less abundant. Because the problem justifies a solution that is precise only to two significant figures, the mass balance equations can be truncated as follows:

$2.0\cdot10^{-7} = [\mathrm{MoO_3S^{2-}}] + [\mathrm{MoO_4^{2-}}]$ (Mo mass balance)

$8.0\cdot10^{-7} = [\mathrm{MoO_3S^{2-}}] + [\mathrm{H_2S}]$ (S mass balance)

Subtracting the first from the second equation and rearranging gives:

$[\mathrm{MoO_4^{2-}}] = [\mathrm{H_2S}] - 6.0\cdot10^{-7}$

Likewise, the S mass balance can be rearranged,

$[\mathrm{MoO_3S^{2-}}] = 8.0\cdot10^{-7} - [\mathrm{H_2S}]$

Employing the equilibrium constant for the reaction involving MoO_4^{2-} and MoO_3S^{2-}:

$$6.5\cdot10^{-6}=\frac{[\mathrm{MoO_4^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoO_3S^{2-}}]}=\frac{([\mathrm{H_2S}]-6.0\cdot10^{-7})\,[\mathrm{H_2S}]}{8.0\cdot10^{-7}-[\mathrm{H_2S}]}$$

Rearrangement and solution by the quadratic formula gives (H_2S). Back substitution gives the remaining concentrations.

Results:

$[\mathrm{H_2S}] = 7.8\cdot10^{-7}$; $[\mathrm{MoO_4^{2-}}] = 1.8\cdot10^{-7}$; $[\mathrm{MoO_3S^{2-}}] = 2.1\cdot10^{-8}$;

$[\mathrm{MoO_2S_2^{2-}}] = 1.0\cdot10^{-9}$; $[\mathrm{MoOS_3^{2-}}] = 8.1\cdot10^{-11}$; $[\mathrm{MoS_4^{2-}}] = 4.9\cdot10^{-12}$.

PROBLEM 7

Diverse permanganatometry

The amount of many reducing agents can be determined by permanganatometric titration in alkaline medium allowing permanganate ion reduction to manganate.

7.1 Write down the ionic reaction equation for titration of formate with permanganate in an aqueous NaOH solution with a concentration of ~0.5 mol dm^{-3}.

Titration with permanganate in alkaline medium is often supplemented by addition of a barium salt, which leads to precipitation of manganate as $BaMnO_4$.

7.2 Which side redox processes involving manganate is suppressed by the barium salt? Write down an example of equation of the corresponding reaction.

A volume of 10.00 cm^3 (V_{Mn}) of $KMnO_4$ solution with a concentration of 0.0400 mol dm^{-3} (c_{Mn}) was placed in each of flasks **A**, **B**, and **C** and different reactions were conducted in each flask.

A sample solution containing crotonic acid (CA) $CH_3–CH=CH–COOH$, an alkali and barium nitrate (both in an excess) were added to flask **A**, and the reaction mixture was incubated for 45 min. It is known that crotonic acid loses 10 electrons under the experiment conditions.

7.3 a Write down the total ionic equation for the reaction.

A volume of 8.00 cm^3 (V_{CN}) of potassium cyanide solution (c_{CN} = 0.0100 mol dm^{-3}) was then added to the incubated mixture. This resulted in completion of the following reaction:

$$2\ Ba^{2+} + 2\ MnO_4^- + CN^- + 2\ OH^- \rightarrow 2\ BaMnO_4 + CNO^- + H_2O$$

$BaMnO_4$ precipitate was then filtered off, and the excess of cyanide in the filtrate was titrated with $AgNO_3$ solution (c_{Ag} = 0.0050 mol dm^{-3}) till detectable precipitation was observed. Note that both CN^- and CNO^- are analogs of halide ions, but CNO^- affords soluble silver salt.

7.3 b Give the formula for the complex formed when Ag^+ ions were initially added to the cyanide solution (until the precipitate was formed).

7.3 c Give the formula of the precipitate formed.

7.3 d Derive the formula for calculating the amount of substance of crotonic acid in the sample solution. Calculate the mass of crotonic acid (in mg) if 5.40 cm^3 (V_{Ag}) of the silver salt solution was consumed for the titration to the endpoint.

Another sample of crotonic acid and alkali (in an excess) were added to flask **B**, this mixture lacking barium salt. An excess of KI (instead of cyanide) was added as a reducing agent. The mixture was then acidified and the iodine evolved was titrated with a thiosulfate solution (c_S = 0.1000 mol dm^{-3}). 4.90 cm^3 (V_{S1}) of the titrant was used to reach the endpoint.

7.4 Derive the formula for calculating the amount of substance of crotonic acid in this experiment. Calculate the mass of crotonic acid (in mg).

A sample containing tin(II) was added to flask **C**, and the medium was adjusted to weak alkaline. Tin(II) was quantitatively oxidized to $Sn(OH)_6^{2-}$, whereas a precipitate formed as a result of permanganate reduction. The precipitate was isolated, washed off, dried at 250 °C, weighed (the mass of the water-free precipitate (m_{prec}), representing a binary compound, was of 28.6 mg), and dissolved in H_2SO_4 in the presence of an excess of potassium iodide. The evolved iodine was titrated with 0.1000 M thiosulfate solution. 2.5 cm^3 (V_{S2}) of the latter was consumed to attain the endpoint.

7.5 a Write down the reaction of precipitation. Confirm it with calculations.

7.5 b Calculate the mass of tin in the sample (in mg) referred to the metal.

SOLUTION

7.1 $2\ MnO_4^- + HCOO^- + 3\ OH^- \rightarrow 2\ MnO_4^{2-} + CO_3^{2-} + 2\ H_2O$

7.2 $MnO_4^{2-} + 2\ H_2O + 2\ e^- \rightarrow MnO_2 + 4\ OH^-$

or

$3\ MnO_4^{2-} + 2\ H_2O \rightarrow MnO_2 + 2\ MnO_4^- + 4\ OH^-$

7.3 a $C_4H_5O_2^- + 10\ MnO_4^- + 14\ OH^- + 12\ Ba^{2+} \rightarrow$

$\rightarrow 10\ BaMnO_4 + CH_3COO^- + 2\ BaCO_3 + 8\ H_2O$

7.3 b Before the endpoint was attained:

$[Ag(CN)_2]^-$

7.3 c After the endpoint:

$Ag^+ + Ag(CN)_2^- = Ag[Ag(CN)_2]\downarrow$ or $Ag^+ + CN^- = AgCN\downarrow$

Thus: $Ag[Ag(CN)_2]$ or AgCN is the correct answer.

7.3 d Permanganate left after the reaction with crotonic acid: $c_{Mn}V_{Mn} – 10\ n_{CA}$ (mmol).

Cyanide consumed for the residual permanganate: $½\ (c_{Mn}V_{Mn} – 10\ n_{CA})$ (mmol).

Cyanide excess: $c_{CN}V_{CN} – ½\ (c_{Mn}V_{Mn} – 10\ n_{CA})$

For the correct silver-cyanide stoichiometry (1 : 2):

$2\ c_{Ag}V_{Ag} = c_{CN}V_{CN} – ½\ (c_{Mn}V_{Mn} – 10\ n_{CA})$.

Thus: $n_{CA} = \dfrac{2\ c_{Ag}V_{Ag} - c_{CN}V_{CN} + ½\ c_{Mn}V_{Mn}}{5}$

$$n_{CA} = \frac{2 \times 0.005 \times 5.40 - 0.0100 \times 8.00 + 0.5 \times 0.0400 \times 10.00}{5} = 0.0348 \text{ mmol,}$$

Then:

$m_{CA} = 0.0348 \times 86.09 = 3.00$ mg   ($M_{CA} = 86.09$ g mol^{-1}).

For the wrong silver-cyanide stoichiometry (1 : 1):

$c_{Ag}V_{Ag} = c_{CN}V_{CN} – ½\ (c_{Mn}V_{Mn} – 10\ n_{CA})$

$$n_{CA} = \frac{c_{Ag}V_{Ag} - c_{CN}V_{CN} + ½\, c_{Mn}V_{Mn}}{5}$$

$$n_{CA} = \frac{0.005 \times 5.40 - 0.0100 \times 8.00 + 0.5 \times 0.0400 \times 10.00}{5} = 0.0290 \text{ mmol}$$

Then:

$m_{CA} = 0.0290 \times 86.09 = 2.49$ mg

7.4 Schematically:

$$10\ MnO_4^- + 1\ \text{Crotonate} \rightarrow 10\ MnO_4^{2-} + \text{ products}$$

Permanganate left after the reaction with crotonic acid: $c_{Mn}V_{Mn} - 10\ n_{CA}$ (mmol)

Manganate formed: $10\ n_{CA}$ (mmol)

Reactions occurred after iodide addition:

$$2\ MnO_4^- + 10\ I^- + 16\ H^+ \rightarrow 2\ Mn^{2+} + 5\ I_2 + 8\ H_2O \text{ and}$$

$$MnO_4^{2-} + 4\ I^- + 8\ H^+ \rightarrow Mn^{2+} + 2\ I_2 + 4\ H_2O$$

Amount of substance of the iodine evolved (mmol I_2):

$$2.5\ n_{KMnO_4 \text{ left}} + 2\ n_{K_2MnO_4} = 2.5\ (c_{Mn}\ V_{Mn} - 10\ n_{CA}) + 2 \times 10\ n_{CA}$$

$2\ Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\ NaI$

$$n_{Na_2S_2O_3} = 2\ n_{I_2} = 5\ (c_{Mn}V_{Mn} - 10\ n_{CA}) + 40\ n_{CA}$$

Thus:

$5\ (c_{Mn}V_{Mn} - 10\ n_{CA}) + 40\ n_{CA} = c_S V_{S1}$,

and

$n_{CA} = ½\ c_{Mn}V_{Mn} - 0.1\ c_S V_{S1}$

$n_{CA} = (0.5 \times 0.0400 \times 10.00) - (0.1 \times 0.1000 \times 4.90) = 0.151$ mmol,

$m_{CA} = n_{CA}\ M_{CA} = 13.00$ mg.

7.5 a Oxidation of tin(II) with permanganate in weak alkaline medium led to an insoluble binary manganese compound. Drying conditions suggest it is either one of manganese oxides or their mixture.

The amount of equivalent is just the same for thiosulfate, iodine and the precipitate.

$n_{eq} = V_{s2}\, c_S = 0.1000 \times 2.5 = 0.25$ mmol

$M_{eq} = 28.6$ mg / 0.25 mmol = 114.4 g mol^{-1}.

This is the so called molar mass of the equivalent of the precipitate.

Let us consider possible cases.

- If MnO_2 was formed

  (scheme: $MnO_4^- + Sn^{2+} \rightarrow MnO_2\downarrow + Sn^{4+}$)

  $MnO_2 + 4\ H^+ + 2\ I^- \rightarrow I_2 + Mn^{2+} + 2\ H_2O$,

  $I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$

  The molar mass of its equivalent in the reaction with iodide would be: 86.94 / 2 = 43.47 g mol^{-1}.
- If Mn_2O_3 was formed ($Mn_2O_3 + 2\ I^- + 6\ H^+ \rightarrow I_2 + 2\ Mn^{2+} + 3\ H_2O$), the molar mass of its equivalent in the reaction with iodide would be: 157.88 / 4 = 78.9 g mol^{-1}.
- In the experiment, the molar mass of the equivalent is even higher, thus manganese compounds not oxidizing iodide, can be present in the precipitate, i. e. manganese(II). The only possible variant is manganese(II, III) oxide ($Mn_3O_4 + 2\ I^- + 8\ H^+ \rightarrow I_2 + 3\ Mn^{2+} + 4\ H_2O$). The molar mass of the latter: 228.9 / 2 = 114.4 g mol^{-1}.

Reaction:

$$6\,MnO_4^- + 13\,[Sn(OH)_4]^{2-} + 16\,H_2O \rightarrow 2\,Mn_3O_4\downarrow + 13\,[Sn(OH)_6]^{2-} + 6\,OH^-$$

7.5 b Amount of substance of tin equals 13 / 2 of that of Mn_3O_4, or

$n_{Sn} = 28.6 / 228.9 \times 13 / 2 = 0.812$ mmol

$m_{Sn} = 96.4$ mg.

Student name **Student code**

Theoretical **Problem 5** **6.5 %** of the total	**Code:**		Question	1	2	3	4	Total
	Examiner		Mark	6	4	4	6	**20**
			Grade					

Problem 5. Acid-base Equilibria in Water

A solution **(X)** contains two weak monoprotic acids (those having *one* acidic proton); HA with the acid dissociation constant of $K_{HA} = 1.74 \times 10^{-7}$, and HB with the acid dissociation constant of $K_{HB} = 1.34 \times 10^{-7}$. The solution **X** has a pH of 3.75.

1. Titration of 100 mL solution **X** requires 100 mL of 0.220 M NaOH solution for completion.

Calculate the initial (total) concentration ($mol \cdot L^{-1}$) of each acid in the solution **X**. Use reasonable approximations where appropriate. [$K_W = 1.00 \times 10^{-14}$ at 298 K.]

Student name **Student code**

2. **Calculate** the pH of the solution **Y** which initially contains 6.00×10^{-2} M of NaA and 4.00×10^{-2} M of NaB.

3. Adding large amounts of distilled water to solution **X** gives a very (infinitely) dilute solution where the total concentrations of the acids are close to zero. **Calculate** the percentage of dissociation of each acid in this dilute solution.

4. A buffer solution is added to solution **Y** to maintain a pH of 10.0. Assume no change in volume of the resulting solution **Z**.

Calculate the solubility (in mol·L^{-1}) of a substance $M(OH)_2$ in **Z**, given that the anions A^- and B^- can form complexes with M^{2+}:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.1 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.0 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^+$ $K'_1 = 6.2 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.3 \times 10^2$

Student name **Student code**

Theoretical **Problem 5** **6.5 %** of the total	**Code:**		Question	1	2	3	4	Total
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1. Titration of 100 mL solution **X** requires 100 mL of 0.220 M NaOH solution for completion.

Calculate the initial (total) concentration (mol·L^{-1}) of each acid in the solution **X**.
Use reasonable approximations where appropriate. [$K_W = 1.00 \times 10^{-14}$ at 298 K.]

Solution: In solution **X**, H$^+$ was produced from the reactions :

$$\mathbf{HA \rightleftharpoons H^+ + A^-} \quad \text{and} \quad \mathbf{HB \rightleftharpoons H^+ + B^-} \quad \text{and} \quad \mathbf{H_2O \rightleftharpoons H^+ + OH^-}$$

The positive and negative charges in an aqueous solution must balance. Thus the charge balance expression is:

$$[OH^-] + [A^-] + [B^-] = [H^+] \qquad \text{(Eq.1)}$$

In the acidic solution (pH = 3.75), [OH$^-$] can be neglected, so:

$$[A^-] + [B^-] = [H^+] \qquad \text{(Eq. 2)}$$

From equilibrium expression: $\dfrac{[H^+]\times[A^-]}{[HA]} = K_{HA}$

and $[HA] = [HA]_i - [A^-]$ (*where $[HA]_i$ is the initial concentration*)

So: $[H^+]\times[A^-] = K_{HA}\times[HA] = K_{HA}\left([HA]_i - [A^-]\right)$

Thus, the equilibrium concentration of [A$^-$] can be presented as:

$$\left[A^-\right] = \frac{K_{HA}\times[HA]_i}{K_{HA}+[H^+]}$$

Similarly, the equilibrium concentration of [B$^-$] can be presented as:

$$\left[B^-\right]=\frac{K_{HB}\times[HB]_i}{K_{HB}+[H^+]}$$

Substitute equilibrium concentrations of $[A^-]$ and $[B^-]$ into Eq.2:

$$\frac{K_{HA}\times[HA]_i}{K_{HA}+[H^+]}+\frac{K_{HB}\times[HB]_i}{K_{HB}+[H^+]}=\left[H^+\right]$$ 2 pts

Since K_{HA}, K_{HB} are much smaller than $[H^+]$, thus:

$$\frac{K_{HA}\times[HA]_i}{[H^+]}+\frac{K_{HB}\times[HB]_i}{[H^+]}=\left[H^+\right]$$

or $1.74\times10^{-7}\times[HA]_i+1.34\times10^{-7}\times[HB]_i=[H^+]^2=(10^{-3.75})^2$

$1.74\times[HA]_i+1.34\times[HB]_i=0.316$ (Eq. 3)

Neutralization reactions show:

$$HA + NaOH \longrightarrow NaA + H_2O$$

$$HB + NaOH \longrightarrow NaB + H_2O$$

$n_{HA}+n_{HB}=n_{NaOH}$

or $([HA]_i+[HB]_i)\times0.1\ L=0.220\ M\times0.1\ L$ 2 pts

$[HA]_i+[HB]_i=0.220\ M$ (Eq. 4)

Solving Eq.3 and Eq.4 gives: $[HA]_i=0.053\ M$ and $[HB]_i=0.167\ M$

Concentration of HA = 0.053 M

Concentration of HB = 0.167 M **2 pts**

2. **Calculate** the pH of the solution **Y** which initially contains 6.00×10^{-2} M of NaA and 4.00×10^{-2} M of NaB.

Solution:

Solution **Y** contains NaA 0.06 M and NaB 0.04 M. The solution is basic, OH^- was produced from the reactions:

$NaA + H_2O \rightleftharpoons HA + OH^-$ $K_{b,A}=K_w/K_{HA}=5.75\times10^{-8}$

$NaB + H_2O \rightleftharpoons HB + OH^-$ $K_{b,B}=K_w/K_{HB}=7.46\times10^{-8}$

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w=1.00\ 10^{-14}$

and we have:

$[H^+] + [HA] + [HB] = [OH^-]$ (Eq. 5)

In the basic solution, $[H^+]$ can be neglected, so:

$[HA] + [HB] = [OH^-]$ (Eq. 6)

From equilibrium expression: $\frac{[OH^-]\times[HA]}{[A^-]} = K_{b,A}$

and $[A^-] = 0.06 - [HA]$ 1 pt

Thus, the equilibrium concentration of HA can be presented as: $[HA] = \frac{K_{b,A}\times 0.06}{K_{b.A} + [OH^-]}$

Similarly, the equilibrium concentration of HB can be presented as: $[HB] = \frac{K_{b,B}\times 0.04}{K_{b.B} + [OH^-]}$

Substitute equilibrium concentrations of HA and HB into Eq. 6:

$$\frac{K_{b,A}\times 0.06}{K_{b.A} + [OH^-]} + \frac{K_{b,B}\times 0.04}{K_{b.B} + [OH^-]} = [OH^-]$$ 2 points

Assume that $K_{b,A}$ and $K_{b,B}$ are much smaller than $[OH^-]$ (*), thus:

$[OH^-]^2 = 5.75 \times 10^{-8} \times 0.06 + 7.46 \times 10^{-8} \times 0.04$

$[OH^-] = 8.02 \times 10^{-5}$ (the assumption (*) is justified)

So pOH = 4.10 and **pH = 9.90** **1 point**

3. Adding large amounts of distilled water to solution **X** gives a very (infinitely) dilute solution where the total concentrations of the acids are close to zero. **Calculate** the percentage of dissociation of each acid in this dilute solution.

Solution: HA in the dilute solution:

$[A^-] = \alpha \times [HA]_i$

$[HA] = (1 - \alpha) \times [HA]_i$

$[H^+] = 10^{-7}$

Substitute these equilibrium concentrations into K_{HA} expression:

$$\frac{10^{-7}\times\alpha\times[HA]_i}{(1-\alpha)\times[HA]_i} = K_{HA} \quad \text{or} \quad \frac{10^{-7}\times\alpha}{(1-\alpha)} = 1.74\times10^{-7}$$ 2 pts

Solving the equation gives: $\alpha = 0.635$

Similarly, for HB: $\frac{10^{-7}\times\alpha}{(1-\alpha)} = 1.34\times10^{-7}$

Solving the equation gives: $\alpha = 0.573$

- The percentage of dissociation of HA = **65.5 %**

- The percentage of dissociation of HB = **57.3 %** **2 points**

4. A buffer solution is added to solution **Y** to maintain a pH of 10.0. Assume no change in volume of the resulting solution **Z**.

Calculate the solubility (in $\text{mol}\cdot\text{L}^{-1}$) of a subtancce $M(OH)_2$ in **Z**, given that the anions A^- and B^- can form complexes with M^{2+}:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.1 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.0 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^+$ $K'_1 = 6.2 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.3 \times 10^2$

Solution:

$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$ $K_{sp} = 3.10 \times 10^{-12}$

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.00 \times 10^{-14}$

$M^{2+} + A^- \rightleftharpoons [MA]^+$ $K_1 = 2.10 \times 10^3$

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ $K_2 = 5.00 \times 10^2$

$M^{2+} + B^- \rightleftharpoons [MB]^+$ $K'_1 = 6.20 \times 10^3$

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ $K'_2 = 3.30 \times 10^2$

Solubility of $M(OH)_2 = s = [M^{2+}] + [MA^+] + [MA_2] + [MB^+] + [MB_2]$

pH of **Z** = 10.0

$$[M^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{3.10 \times 10^{-12}}{(10^{-4})^2} = 3.10 \times 10^{-4}\ \text{M} \qquad \text{Eq.1}$$

At pH = 10.0

$$[A^-]_{total} = \frac{K_{HA} \times 0.06}{(K_{HA} + 10^{-10})} = 0.06$$

$[MA^+] = K_1[M^{2+}][A^-] = 2.1 \times 10^3 \times 3.10 \times 10^{-4} \times [A^-] = 0.651 \times [A^-]$ Eq. 3

$[MA_2] = K_1K_2[M^{2+}][A^-]^2 = 325.5 \times [A^-]^2$ Eq. 4

$[A^-]_{total} = [A^-] + [MA^+] + 2 \times [MA_2] = 0.06$ M Eq. 5

Substitute Eq. 3 and Eq. 4 into Eq. 5:

$[A^-] + 0.651 \times [A^-] + 2 \times 325.5 \times [A^-]^2 = 0.06$ **2 pts**

Solve this equation: $[A^-]$ = $\mathbf{8.42 \times 10^{-3}}$ **M**

Substitute this value into Eq. 3 and Eq. 4:

$[MA^+] = 0.651 \times [A^-] =$ $\mathbf{5.48 \times 10^{-3}}$ **M**

$[MA_2] = 325.5 \times [A^-]^2 =$ $\mathbf{2.31 \times 10^{-2}}$ **M**

Similarly,

$[B^-]_{total} = 0.04$ M

$[MB^+] = K_1'[M^{2+}][B^-] = 6.2\times10^3 \times 3.10\times10^{-4} \times [B^-] = 1.92\times[B^-]$ Eq. 6

$[MB_2] = K_1'K_2'[M^{2+}][B^-]^2 = 634.3\times[B^-]^2$ Eq.7

$[B^-]_{total} = [B^-] + [MB^+] + 2 \times [MB_2] = 0.04$ M Eq. **8** **2pts**

Substitute Eq. 6 and Eq. 7 into Eq. 8:

$[B^-] + 1.92 \times [B^-] + 2 \times 634.3 \times [B^-]^2 = 0.04$

Solve this equation: $\mathbf{[B^-]}$ $\mathbf{= 4.58 \times 10^{-3}}$ **M**

Substitute this value into Eq. 6 and Eq. 7:

$[MB^+] = 1.92 \times [B^-] =$ $\mathbf{8.79 \times 10^{-3}}$ **M**

$[MB_2] = 634.3 \times [B^-]^2 =$ $\mathbf{1.33 \times 10^{-2}}$ **M**

Thus, solubility of $M(OH)_2$ in **Z** is **s’**

s’ = $3.10\times10^{-4} + 5.48\times10^{-3} + 2.31\times10^{-2} + 8.79\times10^{-3} + 1.33\times10^{-2} =$ $\mathbf{5.10\times10^{-2}}$ **M**

Answer: Solubility of $\mathbf{M(OH)_2}$ in Z = $\mathbf{5.10\times10^{-2}}$ M. **2 points**

Problem 3. Two binding centers – competition or cooperation?
(7 points)

Question	1		2				**Total**
	1.1	1.2	2.1	2.2	2.3	2.4	
Marks	3	2	8	3	6	6	**28**

Many chemical reactions in living organisms include the formation of "host-guest" complexes where the host molecule reversibly binds one or several guest molecules. Consider a host molecule $\boldsymbol{H}$ with two binding centers – say, *a* and *b* which have different affinities for the guest molecules $\boldsymbol{G}$:

$$\boldsymbol{H} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_a} \qquad K_a = \frac{[\boldsymbol{HG}_a]}{[\boldsymbol{H}][\boldsymbol{G}]}$$

$$\boldsymbol{H} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_b} \qquad K_b = \frac{[\boldsymbol{HG}_b]}{[\boldsymbol{H}][\boldsymbol{G}]} \qquad K_b \neq K_a.$$

where $\boldsymbol{HG}_\mathbf{a}$ and $\boldsymbol{HG}_\mathbf{b}$ denote a complex where guest is bound to *a* center and *b* center, respectively. K_a and K_b are the binding constants for the centers *a* and *b*, brackets denote molar concentrations.

Attachment of one $\boldsymbol{G}$ molecule to $\boldsymbol{H}$ can change the binding ability of the second centre. This change is described by the "interaction factor" β which reflects the influence of one binding center on another and is defined as follows:

$$\boldsymbol{HG_a} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_2} \qquad \frac{[\boldsymbol{HG}_2]}{[\boldsymbol{HG}_a][\boldsymbol{G}]} = \beta K_b$$

where $\boldsymbol{HG}_\mathbf{2}$ is the completely bound complex.

1.1. Determine the range of values (or one value, if necessary) of β which correspond to three possible ways of interaction between binding centers: a) cooperation (binding by one center facilitates subsequent binding); b) competition (first binding complicates the second); c) independence (no interaction).

Cooperation:

Competition:

Independence:

1.2. Find the equilibrium constant for the process: $HG_b + G \rightleftarrows HG_2$ in terms of binding constant(s) and interaction factor.

Calculations:

K =

2.1. The solution was prepared with the initial concentrations $[H]_0 = 1$ M and $[G]_0 = 2$ M. After the reactions were completed, the concentration of H decreased by 10 times and that of G by 4 times. For these host and guest, $K_b = 2K_a$. Determine the concentrations of all other species in the solution and find the binding constant K_a and the factor β.

Calculations:

$[HG_a]$ =

$[HG_b]$ =

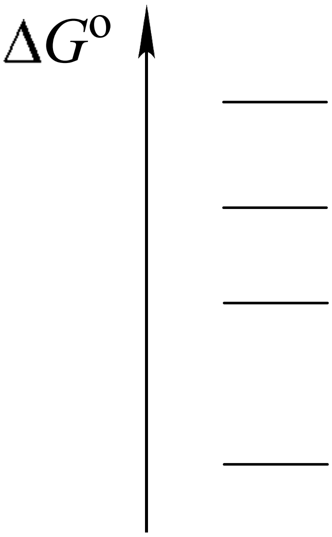
$[HG_2]$ =

K_a =

β =

If you could not answer this question, for further calculations use reference values $K_a = 3.14$ and $\beta = 2.72$.

2.2. Find the correct order of standard molar Gibbs energies of formation of host ***H*** and all host-guest complexes from ***H*** and ***G***. In the scheme below, write the corresponding chemical formula near every line.



2.3. Some amount of ***G*** was added to 1 mole of ***H*** and the mixture was dissolved in water to obtain 1 liter of the solution. The number of the totally bound molecules ***HG*$_2$** in the solution is equal to the total number of single-bound molecules ***HG***. Find the initial amount of ***G*** (in mol). The constants K_a and K_b and the factor β are the same as in question 2.1.

Calculations:

$n_0(G) =$

2.4. What would be the equilibrium composition of the solution if: a) β = 0; b) β is very large (β → ∞). The constants K_a and K_b as well as the initial concentrations of ***H*** and ***G*** are the same as in question 2.1.

β = 0

Calculations:

[***H***] = [***G***] = [$\boldsymbol{HG_a}$] = [$\boldsymbol{HG_b}$] =

[$\boldsymbol{HG_2}$] =

β → ∞

Calculations (or arguments):

[***H***] = [***G***] = [$\boldsymbol{HG_a}$] = [$\boldsymbol{HG_b}$] =

[$\boldsymbol{HG_2}$] =

Problem 3. Two binding centers – competition or cooperation?
(7 points)

Question	1		2				**Total**
	1.1	1.2	2.1	2.2	2.3	2.4	
Marks	3	2	8	3	6	6	**28**

Many chemical reactions in living organisms include the formation of "host-guest" complexes where the host molecule reversibly binds one or several guest molecules. Consider a host molecule ***H*** with two binding centers – say, *a* and *b* which have different affinities for the guest molecules ***G***:

$$\boldsymbol{H} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_a} \qquad K_a = \frac{[\boldsymbol{HG}_a]}{[\boldsymbol{H}][\boldsymbol{G}]}$$

$$\boldsymbol{H} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_b} \qquad K_b = \frac{[\boldsymbol{HG}_b]}{[\boldsymbol{H}][\boldsymbol{G}]} \qquad K_b \neq K_a.$$

where ***HG*a** and ***HG*b** denote a complex where guest is bound to *a* center and *b* center, respectively. K_a and K_b are the binding constants for the centers *a* and *b*, brackets denote molar concentrations.

Attachment of one ***G*** molecule to ***H*** can change the binding ability of the second centre. This change is described by the "interaction factor" β which reflects the influence of one binding center on another and is defined as follows:

$$\boldsymbol{HG_a} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_2} \qquad \frac{[\boldsymbol{HG}_2]}{[\boldsymbol{HG}_a][\boldsymbol{G}]} = \beta K_b$$

where ***HG*₂** is the completely bound complex.

1.1. Determine the range of values (or one value, if necessary) of β which correspond to three possible ways of interaction between binding centers: a) cooperation (binding by one center facilitates subsequent binding); b) competition (first binding complicates the second); c) independence (no interaction).

Cooperation: $\beta > 1$ **1 pt** (**0.5 pt** – for value, not range)
Competition: $0 < \beta < 1$ **1 pt** (**0.5 pt** without zero; **0.5 pt** – for value, not range)
Independence: $\beta = 1$ **1 pt**
Total **3 pts**

1.2. Find the equilibrium constant for the process: $\boldsymbol{HG_b} + \boldsymbol{G} \rightleftarrows \boldsymbol{HG_2}$ in terms of binding constant(s) and interaction factor.

Calculations:

$$K = \frac{[HG_2]}{[HG_b][G]} = \frac{[HG_2]}{[HG_a][G]} \cdot \frac{[HG_a]}{[HG_b]} = \beta K_b \cdot \frac{K_a}{K_b} = \beta K_a$$

$\boldsymbol{K} = \beta K_a$ **2 pts**

2.1. The solution was prepared with the initial concentrations $[\boldsymbol{H}]_0 = 1$ M and $[\boldsymbol{G}]_0 = 2$ M. After the reactions were completed, the concentration of $\boldsymbol{H}$ decreased by 10 times and that of $\boldsymbol{G}$ by 4 times. For these host and guest, $K_b = 2K_a$. Determine the concentrations of all other species in the solution and find the binding constant K_a and the factor β.

Calculations:

From $K_b = 2K_a$ it follows: $[\boldsymbol{HG_b}] = 2[\boldsymbol{HG_a}]$ **1 pt**

Material balance with respect to $\boldsymbol{H}$: $[\boldsymbol{H}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] + [\boldsymbol{HG_2}] = [\boldsymbol{H}]_0 = 1$ M, or

$0.1 + 3[\boldsymbol{HG_a}] + [\boldsymbol{HG_2}] = 1$ M **0.5 pt**

Material balance with respect to $\boldsymbol{G}$: $[\boldsymbol{G}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] + 2[\boldsymbol{HG_2}] = [\boldsymbol{G}]_0 = 2$ M, or

$0.5 + 3[\boldsymbol{HG_a}] + 2[\boldsymbol{HG_2}] = 2$ M. **0.5 pt**

Solving the system of two equations, we find: $[\boldsymbol{HG_a}] = 0.1$ M, $[\boldsymbol{HG_2}] = 0.6$ M, hence $[\boldsymbol{HG_b}] = 0.2$ M.

$$K_a = \frac{[HG_a]}{[H][G]} = \frac{0.1}{0.1\cdot 0.5} = 2$$

$$\beta = \frac{[HG_2]}{[HG_a][G]K_b} = \frac{0.6}{0.1\cdot 0.5\cdot 4} = 3$$

$[\boldsymbol{HG_a}] = 0.1$ M $[\boldsymbol{HG_b}] = 0.2$ M $[\boldsymbol{HG_2}] = 0.6$ M

(**1 pt** for $[\boldsymbol{HG_a}]$, **2 pts** for $[\boldsymbol{HG_2}]$, and $[\boldsymbol{HG_b}]$ is not marked if $[\boldsymbol{HG_b}] = 2[\boldsymbol{HG_a}]$ was given 1 pt, otherwise **1 pt**)

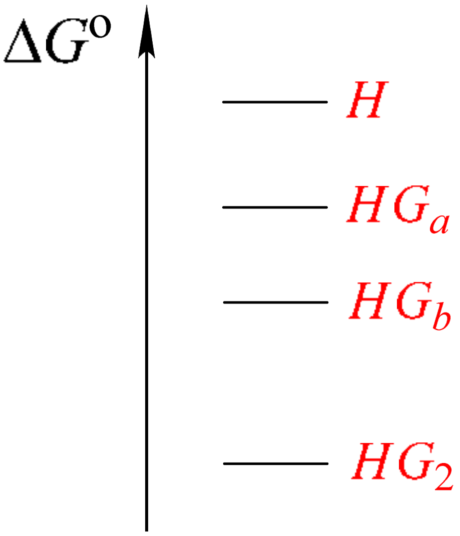
$K_a = 2$ **1 pt**

$\beta = 3$ **2 pts**

Total **8 pts**

If you could not answer this question, for further calculations use reference values $K_a = 3.14$ and $\beta = 2.72$.

2.2. Find the correct order of standard molar Gibbs energies of formation of host $\boldsymbol{H}$ and all host-guest complexes from $\boldsymbol{H}$ and $\boldsymbol{G}$. In the scheme below, write the corresponding chemical formula near every line.



1 pt – for the highest $\Delta G°(\boldsymbol{H})$,
1 pt – for the lowest $\Delta G°(\boldsymbol{HG_2})$
1 pt – for $\Delta G°(\boldsymbol{HG_a}) > \Delta G°(\boldsymbol{HG_b})$

Total **3 pts**

2.3. Some amount of ***G*** was added to 1 mole of ***H*** and the mixture was dissolved in water to obtain 1 liter of the solution. The number of the totally bound molecules $\boldsymbol{HG_2}$ in the solution is equal to the total number of single-bound molecules ***HG***. Find the initial amount of ***G*** (in mol). The constants K_a and K_b and the factor β are the same as in question 2.1.

Calculations:

1) $[HG_2] = [HG_a] + [HG_b] = 3[HG_a]$

$$\frac{[HG_2]}{[HG_a][G]} = \beta K_b = 12, \qquad \frac{3}{[G]} = 12, \qquad [G] = 0.25\text{ M}$$

2) Material balance with respect to H:

$[H] + 3[HG_a] + [HG_2] = 1\text{ M}$
$[H] + 6[HG_a] = 1\text{ M}$
$[H] + 12[H][G] = 1\text{ M}$
$[H] = 0.25\text{ M}.$

3) $[HG_a] = K_a[H]\,[G] = 0.125\text{ M}.$
$[HG_2] = 3[HG_a] = 0.375\text{ M}.$

4) Material balance with respect to G: $[G]_0 = [G] + 3[HG_a] + 2[HG_2] = 1.375\text{ M}$

$n_0(G) = 1.375$ mol

Correct determination of $[G]$, $[H]$, $[HG_a]$, $[HG_2]$ – **1 pt** for each concentration
$n_0(G)$ – **2 pts**

Total **6 pts**

2.4. What would be the equilibrium composition of the solution if: a) β = 0; b) β is very large (β → ∞). The constants K_a and K_b as well as the initial concentrations of ***H*** and ***G*** are the same as in question 2.1.

β = 0

Calculations:

In this case, no $\boldsymbol{HG_2}$ is formed.

Material balance with respect to ***H***: $[H] + [HG_a] + [HG_b] = 1$ M, or

$[H] + 3[HG_a] = 1$ M

Material balance with respect to ***G***: $[G] + [HG_a] + [HG_b] = 2$ M, or

$[G] + 3[HG_a] = 2$ M

Equilibrium constant: $$K_a = \frac{[HG_a]}{[H][G]} = 2$$

Solving the system of three equations, we get:

$[H] = 0.129$ M $[G] = 1.129$ M $[HG_a] = 0.290$ M $[HG_b] = 0.580$ M

$[HG_2] = 0$

1 pt for each concentration except HG_b, maximum – **4 pts**

β → ∞

Calculations (or arguments):

In this case, formation of HG_2 is practically irreversible, so only HG_2 is present in the solution.

$[H] = 0$ $[G] = 0$ $[HG_a] = 0$ $[HG_b] = 0$

$[HG_2] = 1$ M

2 pts

(any calculation which gives similar result – full mark)

Total **6 pts**

Problem 5. Indispensable glucose

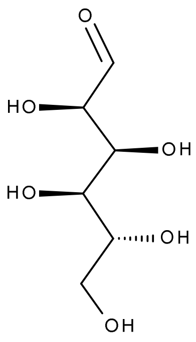
(8 points)

Question	1						2					**Total**
	1.1	1.2	1.3	1.4	1.5	1.6	2.1	2.2	2.3	2.4	2.5	
Marks	2	3	6	4	6	1	2	2	4	2	2	34

Carbohydrates are the most important providers of energy for living cells. Monosaccharide glucose is a source of energy for the living cell, but for persons who suffer from diabetes glucose may be dangerous. High level of glucose may lead to cardiovascular diseases and even death. That is why people avoid consuming too much carbohydrates and glucose particularly.

1. Determination of reducing sugars in fruit juice

One of the technique for determination of reducing sugars in different samples includes the use of Fehling's reagent. A 10.00-mL aliquot of fruit juice (assuming the initial sample contained only glucose and fructose) was transferred into a titration flask and Fehling's reagent was added. This reagent was prepared by mixing 50.00 mL of 0.04000 M copper sulfate (solution A) and potassium-sodium tartrate and sodium hydroxide (solution B). Solution C thus obtained, was then heated and red precipitate was formed.



Glucose

1.1. Write the balanced ionic equation of chemical reaction occurring upon heating of the solution C. Use Cu^{2+} for initial copper solution.

After that 10 mL of 10% solution of potassium iodide and 1 M sulfuric acid were added to the flask. The mixture was covered with watch glass and was then placed in a dark place. An excess of iodine was then titrated with 0.05078 M sodium thiosulphate solution. 11.87 mL of the titrant was required to reach the endpoint.

1.2. Write the balanced equation(s) in molecular or ionic form for all the reactions taking place in the flask.

1.3. Consider all fructose was transformed into glucose under the experimental conditions; calculate the total mass content of sugars (in g/L) in a fruit juice. Mw = 180.16 g/mol.

mass content =

A new 10.00-mL aliquot of the same juice was treated with a 10.00-mL portion of acidified potassium iodate(V) solution (0.01502 M) and 10 mL of 10 % solution of potassium iodide. After the mixture turned brown, an excess of sodium hydroxide solution was added. The flask was then covered with a watch glass and put into a dark place. The obtained solution was acidified and titrated with 0.01089 M solution of sodium thiosulphate. The average titrant volume used for titration was 23.43 mL. Note that fructose is not converted into glucose under these conditions.

1.4. Write all the balanced equations for the described reactions in molecular or ionic form.

1.5. Calculate the mass content of each sugar (in g/L) in the juice.

mass content of glucose =

mass content of fructose =

1.6. One bread exchange unit (1 BEU) corresponds to the content of 12 g of digestible carbohydrates in product. How many BEU are in one glass (200 mL) of juice?

Problem 5. Indispensable glucose

(8 points)

Question	1						2					**Total**
	1.1	1.2	1.3	1.4	1.5	1.6	2.1	2.2	2.3	2.4	2.5	
Marks	2	3	6	4	6	1	2	2	4	2	2	34

Carbohydrates are the most important providers of energy for living cells. Monosaccharide glucose is a source of energy for the living cell, but for persons who suffer from diabetes glucose may be dangerous. High level of glucose may lead to cardiovascular diseases and even death. That is why people avoid consuming too much carbohydrates and glucose particularly.

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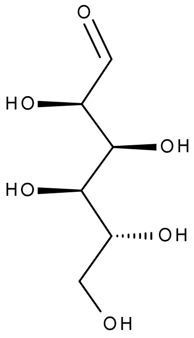


Glucose

1.1. Write the balanced ionic equation of chemical reaction occurring upon heating of the solution C. Use Cu^{2+} for initial copper solution.

$C_6H_{12}O_6 + 2\ Cu^{2+} + 5OH^{-} = C_6H_{11}O_7^{-} + Cu_2O + 3H_2O$ If $C_6H_{12}O_7$ instead of $C_6H_{11}O_7^{-}$ Hereinafter if an equation is not balanced, then points/2.	**2 points** **1 point**

After that 10 mL of 10% solution of potassium iodide and 1 M sulfuric acid were added to the flask. The mixture was covered with watch glass and was then placed in a dark place. An excess of iodine was then titrated with 0.05078 M sodium thiosulphate solution. 11.87 mL of the titrant was required to reach the endpoint.

1.2. Write the balanced equation(s) in molecular or ionic form for all the reactions taking place in the flask.

$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$ or $2Cu^{2+} + 4I^- = 2CuI + I_2$	**2 points**
$KI + I_2 = KI_3$ or $I^- + I_2 = I_3^-$	not marked
$C_6H_{11}O_7^- + H_2SO_4 = C_6H_{12}O_8 + HSO_4^-$	not marked
$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$ or $2S_2O_3^{2-} + I_2 = 2I^- + S_4O_6^{2-}$	**1 point**

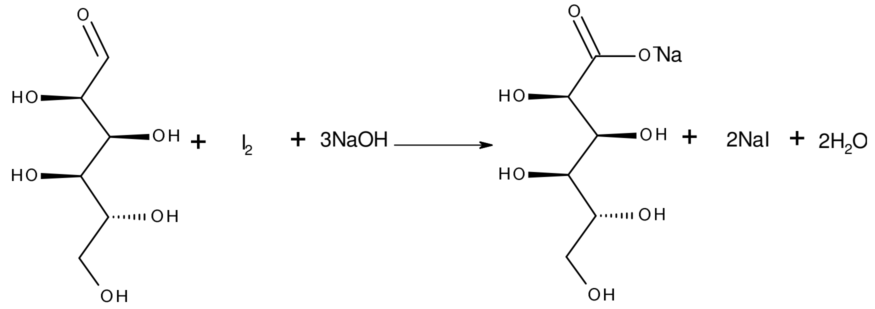
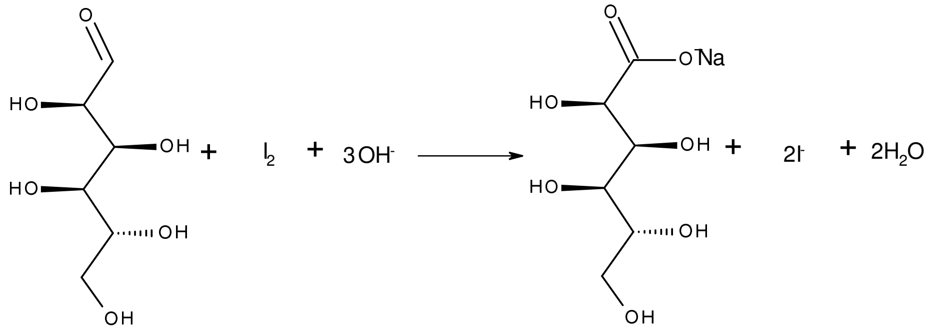
1.3. Consider all fructose was transformed into glucose under the experimental conditions; calculate the total mass content of sugars (in g/L) in a fruit juice. Mw = 180.16 g/mol.

Total amount of copper(II) is 50.00 mL * 0.04000 M = 2.0000 mmol. Obviously, there is an excess of iodine and the remaining iodine was titrated with sodium thiosulphate: 11.87 mL * 0.05078 M = 0.6028 mmol. 2.0000 – 0.6028 mmol = 1.3972 mmol of copper(II) was required to oxidize the sugars. ν(sugars) = $\nu(Cu^{2+})/2$ = 0.6986 mmol in 10.00 mL C(sugars) = 0.6986 mmol/10.00 mL = 0.06986 M mass content = 180.16 g/mol * 0.06986 M = 12.6 g/L	**6 points**

A new 10.00-mL aliquot of the same juice was treated with a 10.00-mL portion of acidified potassium iodate(V) solution (0.01502 M) and 10 mL of 10 % solution of potassium iodide. After the mixture turned brown, an excess of sodium hydroxide solution was added. The flask was then covered with a watch glass and put into a dark place. The obtained solution was acidified and titrated with 0.01089 M solution of sodium thiosulphate. The average titrant volume used for titration was 23.43 mL. Note that fructose is not converted into glucose under these conditions.

1.4. Write all the balanced equations for the described reactions in molecular or ionic form.

$KIO_3 + 5KI + 3H_2SO_4 = 3I_2 + 3K_2SO_4 + 3H_2O$ $IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$	**2 points**
Only glucose was oxidized with iodine	**2 points**

 or 	
$H^+ + OH^- = H_2O$	not marked
$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$	not marked

1.5. Calculate the mass content of each sugar (in g/L) in the juice.

Total amount $\nu(I_2) = 3\nu(IO_3^-) = 3*0.01502$ M * 10 mL = 0.4506 mmol	**1 pt**	**6 points**
$\nu(S_2O_3^{2-})$=23.43 mL*0.01089 M = 0.2552 mmol	**1 pt**	
$\nu(S_2O_3^{2-})/2=\nu(I_2)$ = 0.1276 mmol	**1 pt**	
0.4506 mmol – 0.1276 mmol = 0.3230 mmol of iodine was used to oxidize glucose		
C(glucose) = 0.3230 mmol/10.00 mL = 0.03230 M	**1 pt**	
mass content of glucose = 180.16 g/mol *0.03230 M = 5.82 g/L	**1 pt**	
mass content of fructose = 12.6 – 5.82 = 6.78 g/L	**1 pt**	

1.6. One bread exchange unit (1 BEU) corresponds to the content of 12 g of digestible carbohydrates in product. How many BEU are in one glass (200 mL) of juice?

0.2 L*5.82 g/L = 1.16 g of digestible carbohydrates, it is 0.1 BEU	**1 point**
Or 0.2 L*12.6 g/L = 2.52 g, it is 0.2 BEU	**1 point**

2. Diagnosis of diseases

The derivative of glucose, 2-deoxy-2-(^{18}F)fluoro-D-glucose (FDG), is the most common radiopharmaceuticals for diagnosis of cancer using positron emission tomography. The first step of FDG preparation is to produce a radionuclide fluoro-18 by nuclear reaction in a cyclotron. The next step is the radiochemical synthesis. Fluorine-18 is introduced into D-glucose molecule by

Problem 3 9% of the total

Iodine deficiency is of special concern in Georgia because it occupies a region where iodine is scarce in soil and water. Iodine deficiency can be effectively and inexpensively prevented if salt for human consumption is fortified with small amounts of iodine. Methods for analyzing salt for iodine content are thus important. Current regulations in Georgia are that iodized salt must contain between 25-55 ppm iodine (1 ppm = 1 mg iodine/kg salt).

Most salt is iodized by fortification with potassium iodate (KIO_3). Iodate content can be determined in salt samples using iodometric titration. In a typical procedure, 10.000 g of an iodized salt sample is dissolved in 100 cm^3 of 1.0 mol/dm^3 aqueous HCl to which 1.0 g KI has been added. The solution is then titrated with 0.00235 mol/dm^3 aqueous sodium thiosulfate solution to a starch endpoint; this requires 7.50 cm^3 of titrant.

3.1.1. Write a balanced net ionic equation for the reaction when iodate reacts with excess iodide in acidic solution.

3.1.2. Write a balanced net ionic equation for the reaction taking place during the titration with thiosulfate.

3.1.3. Calculate the iodization level, in ppm, of this salt sample.

A less common agent for iodizing salt is potassium iodide, which cannot be easily measured by iodometric titration.

One possible method for analyzing iodide in the presence of chloride is potentiometric titration. However, this method is not very precise in the presence of large amounts of chloride.

In this method, a silver wire is immersed in the solution (containing iodide and chloride) to be analyzed and silver ion is gradually added to the solution. The potential of the silver wire is measured relative to a reference electrode consisting of a silver wire in a 1.000 mol/dm^3 solution of $AgNO_3$. The measured potentials are negative and the absolute values of these potentials are reported. The solution to be analyzed has a volume of 1.000 dm^3 (which you may assume does not change as silver ion is added), and T = 25.0°C.

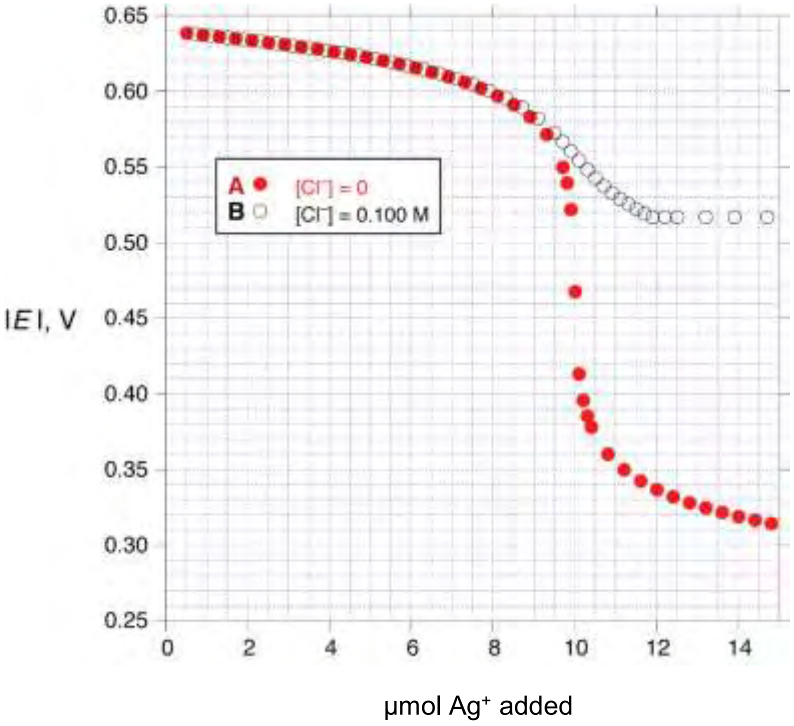
The results of this experiment are governed by three equilibria: the solubility of AgI(s) [K_{spI}] and AgCl(s) [K_{spCl}] and the formation of $AgCl_2^-$(aq) [K_f]. (Iodide also forms complex ions with silver but this may be neglected at the very low concentrations of iodide present in this experiment).

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ K_{spI}

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ K_{spCl}

$Ag^+(aq) + 2\ Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)$ K_f

Below are shown the results of two experiments measuring the observed potential as a function of added number of moles of silver ion. Experiment **A** (solid circles) was carried out with 1.000 dm^3 of solution containing 1.00·10^{-5} mol/dm^3 iodide and no chloride ion. Experiment **B** (open circles) was done using 1.000 dm^3 of solution containing 1.00·10^{-5} mol/dm^3 iodide and 1.00·10^{-1} mol/dm^3 chloride.



μmol Ag$^+$ added	$\lvert E \rvert$, V exp. **A**	$\lvert E \rvert$, V exp. **B**
1.00	0.637	0.637
3.00	0.631	0.631
5.00	0.622	0.622
7.00	0.609	0.610
9.00	0.581	0.584
10.0	0.468	0.558
11.0	0.355	0.531
12.0	0.337	0.517
13.0	0.327	0.517
15.0	0.313	0.517

3.2.1. Select an appropriate data point from the experiments and use it to <u>calculate</u> the solubility product of AgI (K_{spI}).

3.2.2. Select an appropriate data point from the experiments and use it to <u>calculate</u> the solubility product of AgCl (K_{spCl}).

3.2.3. Select an appropriate data point from the experiments and use it to <u>calculate</u> K_f. You may need to use values of K_{spI} or K_{spCl} to do this calculation. If you were unable to carry out the calculations in **3.2.1.** or **3.2.2.**, you may use the arbitrary values of K_{spI} = 1.00·10^{-15} and K_{spCl} = 1.00·10^{-9} without penalty.

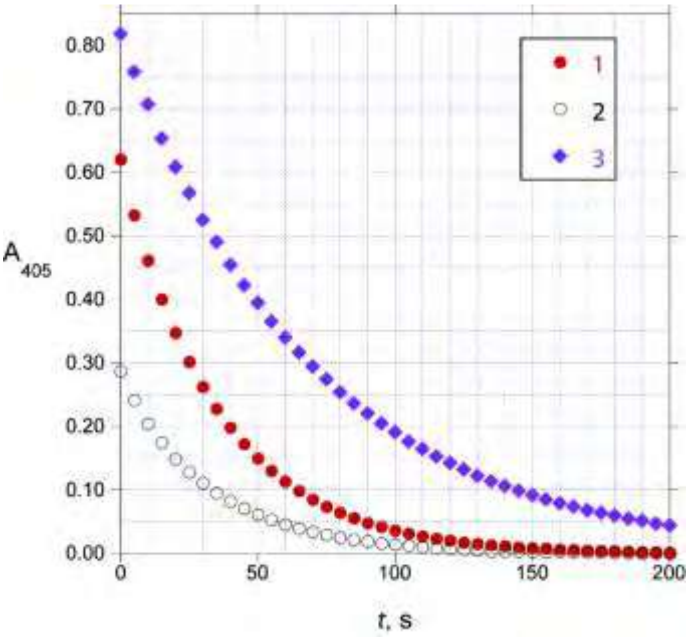
An analytical method that is more practical, because it is not sensitive to the presence of chloride, uses the Sandell-Kolthoff reaction. This is the reaction of H_3AsO_3 with Ce(IV) to give Ce(III) in acidic solution, which is strongly catalyzed by iodide ion.

3.3.1. Write balanced net ionic equations for the reaction of cerium(IV) with H_3AsO_3 in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and H_3AsO_3 with a species containing the element iodine, that could reasonably account for the catalysis of the net reaction by iodide.

The reaction of Ce(IV) with H_3AsO_3 can be monitored by measuring the absorbance at 405 nm, as Ce(IV) is orange and absorbs significantly at 405 nm, while the other reactants and products are colorless and do not absorb appreciably. Three runs were carried out, all in 0.50 mol/dm^3 H_2SO_4 at 25.0°C using the following initial concentrations:

Run	$[H_3AsO_3]_0$, mol dm^{-3}	$[Ce(IV)]_0$, mol dm^{-3}	$[I^-]_0$, mol dm^{-3}
1	0.01250	0.00120	$1.43 \cdot 10^{-6}$
2	0.00625	0.00060	$1.43 \cdot 10^{-6}$
3	0.01250	0.00120	$7.16 \cdot 10^{-7}$

An analyst initiated the reactions by mixing the reagents in a cuvette. After a short variable delay absorbance measurements were started, with the first measurement recorded at t=0 s. The data obtained are shown below:



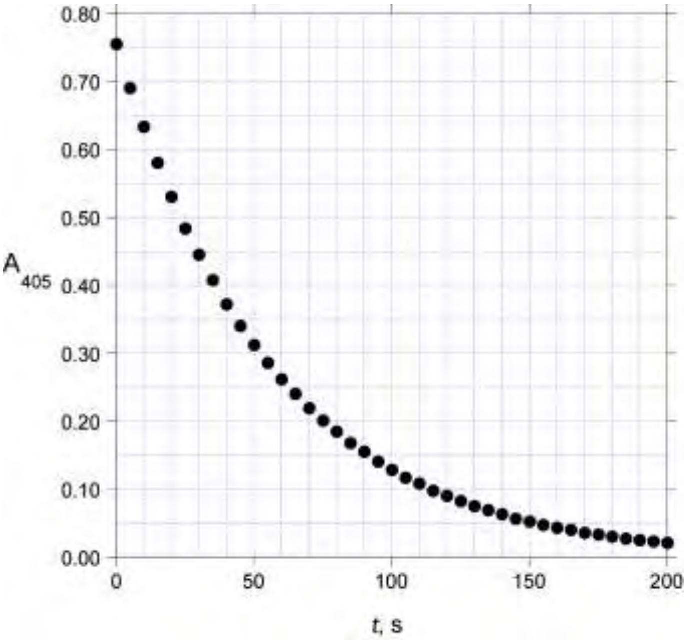
t, s	A_{405} Run **1**	A_{405} Run **2**	A_{405} Run **3**
0	0.621	0.287	0.818
20	0.348	0.149	0.608
40	0.198	0.083	0.455
60	0.113	0.046	0.340
80	0.064	0.025	0.254
100	0.037	0.014	0.191

Under these conditions (0.5 mol/dm^3 H_2SO_4, 25.0°C), the rate law for the reaction can be written as

Rate = $k[H_3AsO_3]^m[Ce(IV)]^n[I^-]^p$ where m, n, and p are integers.

3.3.2. Determine the values of m, n, and p and calculate the value of k (be sure to specify its units).

A 1.000 g sample of iodized salt is dissolved in water to give 10.00 cm^3 of solution. A 0.0500 cm^3 aliquot of this solution is added to a mixture of 1.000 cm^3 0.025 mol/dm^3 H_3AsO_3 in 0.5 mol/dm^3 H_2SO_4 and 0.800 cm^3 0.5 mol/dm^3 H_2SO_4. To this mixture is added 0.200 cm^3 0.0120 mol/dm^3 $Ce(NH_4)_2(NO_3)_6$ in 0.5 mol/dm^3 H_2SO_4 and the absorbance at 405 nm is measured as a function of time at 25.0°C:



t, s	A_{405}
0	0.756
20	0.531
40	0.373
60	0.262
80	0.185
100	0.129

3.3.3. Calculate the iodization level, in ppm, of this salt sample.

Problem 3 9% of the total

3.1.1.	3.1.2.	3.1.3.	3.2.1.	3.2.2.	3.2.3.	3.3.1.	3.3.2.	3.3.3.	Sum
2	2	6	5	4	7	6	11	5	48

3.1.1. Write a balanced net ionic equation for the reaction when iodate reacts with excess iodide in acidic solution.

$IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O$ or $IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$

2p (1p species, 1p coefficients, 0.5p penalty if spectator ions are included.)

3.1.2. Write a balanced net ionic equation for the reaction taking place during the titration with thiosulfate.

$I_3^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_4O_6^{2-}$ or $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

2p (1p species, 1p coefficients, 0.5p penalty if spectator ions are included.)

3.1.3. Calculate the iodization level, in ppm, of this salt sample.

Your work:

$(0.00750\ dm^3$ titrant$)\cdot(0.00235\ mol\ dm^{-3}\ S_2O_3^{2-}) = 1.76\cdot10^{-5}\ mol\ S_2O_3^{2-}$

$(1.76\cdot10^{-5}\ mol\ S_2O_3^{2-})\cdot(1\ mol\ IO_3^-/6\ mol\ S_2O_3^{2-}) = 2.94\cdot10^{-6}\ mol\ IO_3^-$

$(2.94\cdot10^{-6}\ mol\ IO_3^-)\cdot(126.90\ g/mol) = 3.73\cdot10^{-4}$ g iodine

$\{(3.73\cdot10^{-4}$ g iodine$)/(10.00$ g salt$)\}\cdot10^6$ ppm = 37.3 ppm iodine

2p for calculating mol thiosulfate

2p for calculating mol iodate

2p for converting to ppm

ppm iodine =

3.2.1. Select an appropriate data point from the experiments and use it to calculate the solubility product of AgI (K_{spI}).

Your work:

In the experiments, $|E| = -(RT/nF)\ln([Ag^+]_{cell}/[Ag^+]_{ref}) = -0.0591 \cdot \log[Ag^+]$

There is a sharp endpoint at n(added Ag^+) = n (I^- initially present) in experiment **A** ($[Cl^-] = 0$), so precipitation of AgI(s) must be essentially complete at any point in the titration curve. If one considers, for example, 5.0 μmol added Ag^+, then

$[I^-] = [I^-]_0 - 5.0 \cdot 10^{-6}$ mol/dm^3 = $5.0 \cdot 10^{-6}$ mol/dm^3

$|E| = 0.622$ V $= -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 3.2 \cdot 10^{-11}$ mol/dm^3

$K_{spI} = [Ag^+][I^-] = 1.6 \cdot 10^{-16}$

2p for relationship between E and $[Ag^+]$ (full credit if used even if not stated explicitly)

1p for selecting a data point with $n(Ag^+) \leq 10.0$ μmol

2p for calculation of K_{spI}

Full marks are awarded here and later for correct answers with numerical differences stemming from using different data points or minor rounding

K_{spI}:

3.2.2. Select an appropriate data point from the experiments and use it to calculate the solubility product of AgCl (K_{spCl}).

Your work:

In the titration with $[Cl^-] = 0.100$ mol/dm^3 (experiment **B**), the fact that the potential stops changing at n(added Ag^+) ≥ 11.8 μmol must be due to the precipitation of AgCl(s) (the high concentration of chloride therefore effectively fixes the $[Ag^+]$ in the solution). So in this regime:

$|E| = 0.517$ V $= -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 1.6 \cdot 10^{-9}$ mol/dm^3

$K_{spCl} = [Ag^+][Cl^-] = 1.6 \cdot 10^{-10}$

1p for selecting a data point with $n(Ag^+) > 11.8$ μmol

3p for calculation of K_{spCl}

K_{spCl}:

3.2.3. Select an appropriate data point from the experiments and use it to calculate K_f. You may need to use values of K_{spI} or K_{spCl} to do this calculation. If you were unable to carry out the calculations in **3.2.1.** or **3.2.2.**, you may use the arbitrary values of $K_{spI} = 1.00 \cdot 10^{-15}$ and $K_{spCl} = 1.00 \cdot 10^{-9}$ without penalty.

Your work:

There are a number of good approaches to this problem.

One can use the point at which AgCl(s) first precipitates (estimated at 11.8 µmol Ag^+ added) to calculate K_f. At this point, $[Ag^+] = 1.6 \cdot 10^{-9}$ mol/dm³, $[Cl^-] = 0.100$ mol/dm³ (see above).
Almost all of the originally present $1.0 \cdot 10^{-5}$ mol/dm³ iodide has been precipitated out as 9.9 µmol AgI, since $[I^-] = K_{spI}/[Ag^+] = 1.0 \cdot 10^{-7}$ mol/dm³

Total Ag in solution = 11.8 µmol – 9.9 µmol = 1.9 µmol

$[AgCl_2^-] = 1.9 \cdot 10^{-6}$ mol/dm³ (since free $[Ag^+]$ is only $1.6 \cdot 10^{-9}$ mol/dm³)

$$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{1.9 \cdot 10^{-6}}{1.6 \cdot 10^{-9} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [1.9 \cdot 10^4 \text{ given const.}]$$

Same approach works for 11 µmol Ag^+ added.

2p for selecting a data point between 10-12.0 µmol

3p for reasonable method of calculating K_f

2p for value of K_f

An alternative approach is to look at the equivalence point, where

$|E| = 0.558 \text{ V} = -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 3.62 \cdot 10^{-10}$ mol/dm³

Since AgI(*s*) is present, $[I^-] = K_{spI}/[Ag^+] = 4.42 \cdot 10^{-7}$ mol/dm³

The amount of dissolved iodine and silver is equivalent:

$[I^-] = [Ag^+] + [AgCl_2^-] \Rightarrow [AgCl_2^-] = 4.42 \cdot 10^{-7}$ mol/dm³

$$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{4.42 \cdot 10^{-7}}{3.62 \cdot 10^{-10} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [7.6 \cdot 10^5 \text{ given const.}]$$

K_f:

3.3.1. Write balanced net ionic equations for the reaction of cerium(IV) with H_3AsO_3 in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and H_3AsO_3 with a species containing the element iodine, that could reasonably account for the catalysis of the net reaction by iodide.

Net reaction of cerium(IV) with H_3AsO_3 in acidic solution:

$2\ Ce^{4+} + H_3AsO_3 + H_2O \rightarrow 2\ Ce^{3+} + H_3AsO_4 + 2\ H^+$

2p (1p for H_3AsO_3/H_3AsO_4 couple, 1p balanced)

Reaction of cerium(IV) with an iodine-containing species:

$2\ Ce^{4+} + 2\ I^- \rightarrow 2\ Ce^{3+} + I_2$

2p (1p species, 1p balanced). Full marks for I_3^- or I· as products

Reaction of H_3AsO_3 with an iodine-containing species:

$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2\ I^- + 2\ H^+$

2p (1p species, 1p balanced). Full marks for I_3^- or I·as products

Two iodine-containing reactions must add up to the net reaction, otherwise –2p for the iodine-containing reactions

3.3.2. Determine the integer values of *m*, *n*, and *p* and calculate the value of *k* (be sure to specify its units).

Your work:

The limiting reactant is Ce(IV) which is < 10% of the concentration of H_3AsO_3, so only the concentration of Ce(IV) changes appreciably over the course of the reaction. (I^- is a catalyst and is not consumed.) So the order in Ce(IV) can be judged by the time course of the reaction. By eye, it appears to be first order.

This can be verified by calculating $-\ln(A/A_0)\cdot(1/t)$, which should be a constant (k_{obs}) if the reaction is first-order:

t, s	k_{obs}, s^{-1}, Run **1**	k_{obs}, s^{-1}, Run **2**	k_{obs}, s^{-1}, Run **3**
20	0.0290	0.0328	0.0148
40	0.0286	0.0310	0.0147
60	0.0284	0.0305	0.0146
80	0.0284	0.0305	0.0146
100	0.0282	0.0302	0.0145
avg.	0.0285	0.0310	0.0146

So $n = 1$.

Since k_{obs} is unchanged (within 10%) from run **1** to run **2** despite decreasing $[H_3AsO_3]$ by a factor of two, $m = 0$.

In contrast, decreasing $[I^-]$ by a factor of two from run **1** to run **3** results in a decrease in observed rate constant of a factor of two, so $p = 1$.

$k = k_{obs}/[I^-]$, giving values of $1.99\cdot10^4$, $2.17\cdot10^4$, and $2.04\cdot10^4$ dm^3 mol^{-1} s^{-1} for runs **1**-**3**; average $k = 2.07\cdot10^4$ dm^3 mol^{-1} s^{-1}.

4p for documenting 1st-order in Ce(IV), 2p each for m and p,

2p for value of k, 1p for unit of k consistent with given rate law

m = n = p = k =

3.3.3. Calculate the iodization level, in ppm, of the salt sample.

Your work:

t, s	$-\ln(A/A_0)\cdot(1/t)$, s^{-1}
20	0.0177
40	0.0177
60	0.0177
80	0.0176
100	0.0177

So $k_{obs} = 0.0177$ s^{-1} $= k[I^-] = (2.07\cdot10^4$ dm^3 mol^{-1} s$^{-1})[I^-]$

$[I^-] = 8.55\cdot10^{-7}$ mol/dm^3

Since the salt solution was diluted by a factor of (2.05 cm^3)/(0.050 cm^3) = 41, the concentration in the original salt solution was $41\cdot(8.55\cdot10^{-7}$ mol/dm$^3) = 3.51\cdot10^{-5}$ mol/dm^3.

$(3.51\cdot10^{-5}$ mol dm$^{-3})(0.01000$ dm$^3) = 3.51\cdot10^{-7}$ mol I in the salt sample
$(3.51\cdot10^{-7}$ mol iodine$)(126.90$ g/mol$) = 4.45\cdot10^{-5}$ g iodine
$\{(4.45\cdot10^{-5}$ g iodine$)/(1.000$ g salt$)\}\cdot10^6$ ppm = 44.5 ppm I

2p for calculating k_{obs}, 1p for $[I^-]$ from k_{obs}, 2p for converting to ppm

ppm I =

Problem 4

5% of the total

Problem 4	A				Total
	A1	A2	A3	A4	
Total	4	1	5	6	16
Score					

Problem 4: Electrochemistry

Part A. Galvanic cell

The experiment is performed at 30.00°C. The electrochemical cell is composed of a hydrogen half-cell [Pt(*s*)│H_2(*g*)│H^+(*aq*)] containing a metal platinum electrode immersed in a buffer solution under a pressure of hydrogen gas. This hydrogen half-cell is connected to a half-cell of a metal (**M**) strip dipped in an unknown concentration of **M**$^{2+}$(*aq*) solution. The two half-cells are connected *via* a salt bridge as shown in Figure 1.

Note: The standard reduction potentials are given in Table 1.

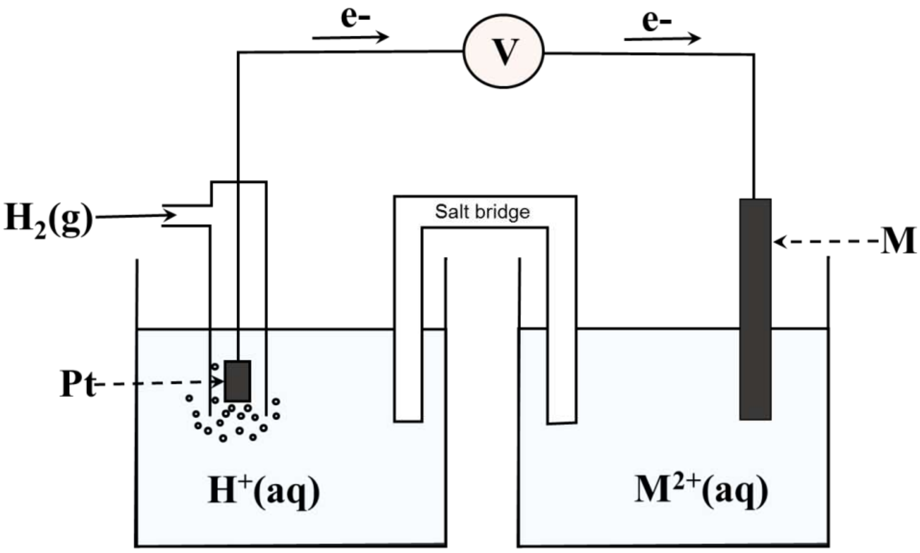


Figure 1 The galvanic cell

Table 1. Standard reduction potential (range 298-308 K)

Half-reaction			**E° (V)**
$Ba^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ba(s)$	-2.912
$Sr^{2+}(aq) + 2e^-$	$\longrightarrow$	$Sr(s)$	-2.899
$Ca^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ca(s)$	-2.868
$Er^{2+}(aq) + 2e^-$	$\longrightarrow$	$Er(s)$	-2.000
$Ti^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ti(s)$	-1.630
$Mn^{2+}(aq) + 2e^-$	$\longrightarrow$	$Mn(s)$	-1.185
$V^{2+}(aq) + 2e^-$	$\longrightarrow$	$V(s)$	-1.175
$Cr^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cr(s)$	-0.913
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow$	$Fe(s)$	-0.447
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cd(s)$	-0.403
$Co^{2+}(aq) + 2e^-$	$\longrightarrow$	$Co(s)$	-0.280
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ni(s)$	-0.257
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow$	$Sn(s)$	-0.138
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow$	$Pb(s)$	-0.126
$2H^+(aq) + 2e^-$	$\longrightarrow$	$H_2(g)$	0.000
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow$	$Sn^{2+}(aq)$	+0.151
$Cu^{2+}(aq) + e^-$	$\longrightarrow$	$Cu^+(aq)$	+0.153
$Ge^{2+}(aq) +2e^-$	$\longrightarrow$	$Ge(s)$	+0.240
$VO^{2+}(aq) + 2H^+(aq) +e^-$	$\longrightarrow$	$V^{3+}(aq) + H_2O(l)$	+0.337
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cu(s)$	+0.340
$Tc^{2+}(aq) + 2e^-$	$\longrightarrow$	$Tc(s)$	+0.400
$Ru^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ru(s)$	+0.455
$I_2(s) + 2e^-$	$\longrightarrow$	$2I^-(aq)$	+0.535
$UO_2^{2+}(aq) + 4H^+(aq)+ 2e^-$	$\longrightarrow$	$U^{4+}(aq) + 2H_2O(l)$	+0.612
$PtCl_4^{2-}(aq) + 2e^-$	$\longrightarrow$	$Pt(s) + 4Cl^-(aq)$	+0.755
$Fe^{3+}(aq) + e^-$	$\longrightarrow$	$Fe^{2+}(aq)$	+0.770
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow$	$2Hg(l)$	+0.797
$Hg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Hg(l)$	+0.851
$2Hg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Hg_2^{2+}(aq)$	+0.920
$Pt^{2+}(aq) + 2e^-$	$\longrightarrow$	$Pt(s)$	+1.180
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow$	$Mn^{2+}(aq) + 2H_2O(l)$	+1.224
$Cr_2O_7^{2-}(aq)+ 14H^+(aq) + 6e^-$	$\longrightarrow$	$2Cr^{3+} (aq) + 7H_2O (l)$	+1.360
$Co^{3+}(aq) + e^-$	$\longrightarrow$	$Co^{2+}(aq)$	+1.920
$S_2O_8^{2-}(aq) + 2e^-$	$\longrightarrow$	$2SO_4^{2-}(aq)$	+2.010

4-A1) If the reaction quotient (Q) of the whole galvanic cell is equal to 2.18 x 10^{-4} at 30.00°C, the electromotive force is +0.450 V. Calculate the value of standard reduction potential (E°) and identify the metal "**M**".

Note; $\Delta G = \Delta G^{o} + RT \ln Q$

Calculations

The standard reduction potential of **M** is ……...………..………V
(Answer with 3 digits after decimal point)

Therefore, the metal "**M**" strip is …………..………

4-A2) Write the balanced equation of the spontaneous redox reaction of the galvanic cell.

4-A3) The unknown concentration of **M**$^{2+}$(*aq*) solution in the cell (Figure 1) can be analyzed by iodometric titration. A 25.00 cm^3 aliquot of **M**$^{2+}$(*aq*) solution is added into a conical flask and an excess of KI added. 25.05 cm^3 of a 0.800 mol dm^{-3} sodium thiosulfate is required to reach the equivalent point. Write all the redox reactions associated with this titration and calculate the concentration of **M**$^{2+}$(*aq*) solution.

Calculations

The concentration of **M**$^{2+}$(*aq*) solution is………………mol dm^{-3}

(answer with 3 digits after decimal point)

If student cannot find the answer, the student can use 0.950 mol dm^{-3} as the concentration of **M**$^{2+}$ for further calculations.

4-A4) In Figure 1, if the hydrogen half-cell is under 0.360 bar hydrogen gas and the platinum electrode is immersed in a 500 cm^3 buffer solution containing 0.050 mol lactic acid ($HC_3H_5O_3$) and 0.025 mol sodium lactate ($C_3H_5O_3Na$), the electromotive force of the galvanic cell measured is +0.534 V. Calculate the pH of the buffer solution and the dissociation constant (K_a) of lactic acid at 30.00°C.

Calculations of pH of the buffer solution

pH of the buffer solution is ……………………………………

(answer with 2 digits after decimal point)

If student cannot find the answer, the student can use 3.46 as the buffer pH for further calculations.

Calculations of the dissociation constant (K_a) of lactic acid

The dissociation constant of lactic acid is ……………………………………

Problem 4

5% of the total

	A1	A2	A3	A4	
Total	4	1	5	6	16
Score					

Problem 4: Electrochemistry

Part A. Galvanic cell

The experiment is performed at 30.00°C. The electrochemical cell is composed of a hydrogen half-cell [Pt(*s*)│H_2(*g*)│H^+(*aq*)] containing a metal platinum electrode immersed in a buffer solution under a pressure of hydrogen gas. This hydrogen half-cell is connected to a half-cell of a metal (**M**) strip dipped in an unknown concentration of $\mathbf{M}^{2+}$(*aq*) solution. The two half-cells are connected *via* a salt bridge as shown in Figure 1.

Note: The standard reduction potentials are given in Table 1.

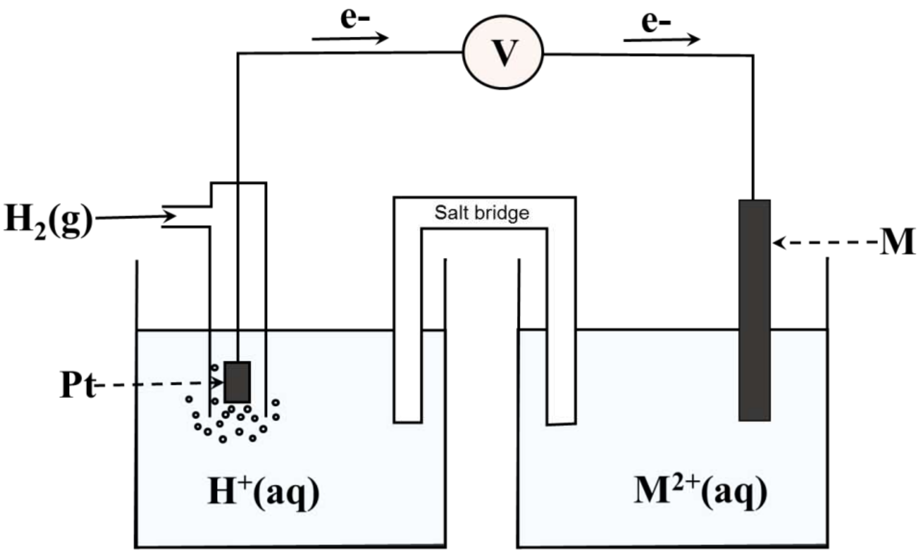


Figure 1 The galvanic cell

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$Fe^{2+}(aq) + 2e^-$	$\longrightarrow$	$Fe(s)$	-0.447
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cd(s)$	-0.403
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$Ni^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ni(s)$	-0.257
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow$	$Sn(s)$	-0.138
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow$	$Pb(s)$	-0.126
$2H^+(aq) + 2e^-$	$\longrightarrow$	$H_2(g)$	0.000
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow$	$Sn^{2+}(aq)$	+0.151
$Cu^{2+}(aq) + e^-$	$\longrightarrow$	$Cu^+(aq)$	+0.153
$Ge^{2+}(aq) +2e^-$	$\longrightarrow$	$Ge(s)$	+0.240
$VO^{2+}(aq) + 2H^+(aq) +e^-$	$\longrightarrow$	$V^{3+}(aq) + H_2O(l)$	+0.337
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow$	$Cu(s)$	+0.340
$Tc^{2+}(aq) + 2e^-$	$\longrightarrow$	$Tc(s)$	+0.400
$Ru^{2+}(aq) + 2e^-$	$\longrightarrow$	$Ru(s)$	+0.455
$I_2(s) + 2e^-$	$\longrightarrow$	$2I^-(aq)$	+0.535
$UO_2^{2+}(aq) + 4H^+(aq)+ 2e^-$	$\longrightarrow$	$U^{4+}(aq) + 2H_2O(l)$	+0.612
$PtCl_4^{2-}(aq) + 2e^-$	$\longrightarrow$	$Pt(s) + 4Cl^-(aq)$	+0.755
$Fe^{3+}(aq) + e^-$	$\longrightarrow$	$Fe^{2+}(aq)$	+0.770
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow$	$2Hg(l)$	+0.797
$Hg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Hg(l)$	+0.851
$2Hg^{2+}(aq) + 2e^-$	$\longrightarrow$	$Hg_2^{2+}(aq)$	+0.920
$Pt^{2+}(aq) + 2e^-$	$\longrightarrow$	$Pt(s)$	+1.180
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow$	$Mn^{2+}(aq) + 2H_2O(l)$	+1.224
$Cr_2O_7^{2-}(aq)+ 14H^+(aq) + 6e^-$	$\longrightarrow$	$2Cr^{3+} (aq) + 7H_2O (l)$	+1.360
$Co^{3+}(aq) + e^-$	$\longrightarrow$	$Co^{2+}(aq)$	+1.920
$S_2O_8^{2-}(aq) + 2e^-$	$\longrightarrow$	$2SO_4^{2-}(aq)$	+2.010

4-A1) If the reaction quotient (Q) of the whole galvanic cell is equal to 2.18 x 10^{-4} at 30.00°C, the electromotive force is +0.450 V. Calculate the value of standard reduction potential (E°) and identify the metal "**M**".

Note; $\Delta G = \Delta G^{o} + RT \ln Q$

Calculations

$$E_{cell} = E^{\circ}_{cell} - (RT/nF)\ \ln\ Q$$

$$+0.450 = E^{\circ}_{cell} - \frac{(8.314\ J\ K^{-1}\ mol^{-1}) \times (303.15\ K)}{2 \times 96485\ C\ mol^{-1}} \ln 2.18 \times 10^{-4} \quad (1\ points)$$

$$+0.450 = E^{\circ}_{cell} + 0.110, \quad (0.5\ point)$$

then $E^{\circ}_{cell} = +0.450\ V - 0.110\ V = +0.340\ V$ *(0.5 point)*

Therefore, $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$+0.340\ V = E^{\circ}_{cathode} - 0.000\ V$; $E^{\circ}_{cathode} = +0.340\ V$ *(0.5 point)*

The standard reduction potential of **M** is ……....+0.340……..………V *(0.5 point)*
(answer with 3 digits after decimal point)

Therefore, the metal "**M**" strip is …………..Cu(s)……… *(1 point)*

or

Calculations

$$E_{cell} = E^{\circ}_{cell} - (2.303RT/nF)\ \log\ Q$$

$$+0.450 = E^{\circ}_{cell} - 2.303\,\frac{(8.314\ J\ K^{-1}\ mol^{-1}) \times (303.15\ K)}{2 \times 96485\ C\ mol^{-1}} \log 2.18 \times 10^{-4}$$

$$+0.450 = E^{\circ}_{cell} + 0.110,$$

then $E^{\circ}_{cell} = +0.450\ V - 0.110\ V = +0.340\ V$

Therefore; $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$+0.340\ V = E^{\circ}_{cathode} - 0.000\ V$; $E^{\circ}_{cathode} = +0.340\ V$

*The standard reduction potential of **M** is ……....+0.340………………………. V*
(Answer with 3 digits after decimal point)

*Therefore, the metal "**M**" strip is ……………Cu(s)………………….*

4-A2) Write the balanced equation of the spontaneous redox reaction of the galvanic cell.

$H_2(g) + Cu^{2+}(aq) \longrightarrow 2H^+(aq) + Cu(s)$ (1 point)

*1 point for correct balanced equation.If students choose a wrong metal (**M**) from **4-A1** but they write the correct balanced equation, they still get 1 point.*

4-A3) The unknown concentration of **M**$^{2+}$(*aq*) solution in the cell (Figure 1) can be analyzed by iodometric titration. A 25.00 cm^3 aliquot of **M**$^{2+}$(*aq*) solution is added into a conical flask and an excess of KI added. 25.05 cm^3 of a 0.800 mol dm^{-3} sodium thiosulfate is required to reach the equivalent point. Write all the redox reactions associated with this titration and calculate the concentration of **M**$^{2+}$(*aq*) solution.

Calculations

Iodometric titration of copper is based on the oxidation of iodide to iodine by copper (II) ions

Reactions taking place,

$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$ *(1 point)*

This is followed during titration by the reaction of iodine with the thiosulfate:

$2Na_2S_2O_3(aq) + I_2(aq) \longrightarrow Na_2S_4O_6(aq) + 2NaI(aq)$ *(1 point)*

or $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$ *(1 point)*

$I_2(aq) + I^-(aq) \longrightarrow I_3^-(aq)$

$I_3^-(aq) + 2Na_2S_2O_3(aq) \longrightarrow Na_2S_4O_6(aq) + 2NaI(aq) + I^-(aq)$ *(1 point)*

At equivalent point,

mol of Cu^{2+} = *mol of* $S_2O_3^{2-}$ *(1 point)*

$(C_{Cu^{2+}} \times V_{Cu^{2+}}/1000) = (C_{S_2O_3^{2-}} \times V_{S_2O_3^{2-}}/1000)$

$C_{Cu^{2+}} = (0.800 \text{ mol dm}^{-3} \times 25.05 \text{ cm}^3)/25.00 \text{ cm}^3$ *(1 point)*

$C_{Cu^{2+}} = 0.802 \text{ mol dm}^{-3}$ *(0.5 point)*

The concentration of **M**$^{2+}$(*aq*) solution is…… *0.802* …….mol dm^{-3} *(0.5 point)*

(answer with 3 digits after decimal point)

If student cannot find the answer, the student can use 0.950 mol dm^{-3} as the concentration of **M**$^{2+}$ for further calculations.

4-A4) In Figure 1, if the hydrogen half-cell is under 0.360 bar hydrogen gas and the platinum electrode is immersed in a 500 cm^3 buffer solution containing 0.050 mol lactic acid ($HC_3H_5O_3$) and 0.025 mol sodium lactate ($C_3H_5O_3Na$), the electromotive force of the galvanic cell measured is +0.534 V. Calculate the pH of the buffer solution and the dissociation constant (K_a) of lactic acid at 30.00°C.

Calculations of pH of the buffer solution

From the Nernst's equation:

$$E_{cell} = E^{\circ}_{cell} - (RT/nF)\ \ln\ ([H^+]^2/P_{H2} \times [Cu^{2+}])$$

$$+0.534\ V = +0.340\ V - \frac{(8.314\ J\ K^{-1}\ mol^{-1}) \times (303.15\ K)}{2 \times 96485\ C\ mol^{-1}}\ \ln \frac{[H^+]^2}{(0.360\ bar) \times (0.802\ mol\ dm^{-3})} \quad (1\ point)$$

$$-14.9 = \ln \frac{[H^+]^2}{(0.360\ bar) \times (0.802\ mol\ dm^{-3})}$$

$$3.52 \times 10^{-7} = \frac{[H^+]^2}{(0.360\ bar) \times (0.802\ mol\ dm^{-3})} \quad (1\ point)$$

$$[H^+] = 3.19 \times 10^{-4} \quad (0.5\ point)$$

$$pH = 3.50$$

pH of the buffer solution is ……………….3.50…………………… *(0.5 point)*

(answer with 2 digits after decimal point)

or

$$E_{cell} = E^{\circ}_{cell} - (2.303\ RT/nF)\ \log\ ([H^+]^2/P_{H2} \times [Cu^{2+}])$$

$$+0.534\ V = +0.340\ V - \frac{2.303 \times (8.314\ J\ K^{-1}\ mol^{-1}) \times (303.15\ K)}{2 \times 96485\ C\ mol^{-1}}\ \log \frac{[H^+]^2}{(0.360\ bar) \times (0.802\ mol\ dm^{-3})}$$

$$-6.45 = \log \frac{[H^+]^2}{(0.360\ atm) \times (0.802\ mol\ dm^{-3})}$$

$$3.53 \times 10^{-7} = \frac{[H^+]^2}{(0.360\ atm) \times (0.802\ mol\ dm^{-3})}$$

$$[H^+] = 3.19 \times 10^{-4}$$

$$pH = 3.50\ (2\ digits)$$

pH of the buffer solution is ……………….3.50…………………………

(Answer with 2 digits after decimal point)

If student cannot find the answer, the student can use 3.46 as the buffer pH for further calculations.

Calculations of the dissociation constant (K_a) of lactic acid

The buffer solution composes of $HC_3H_5O_3$ and $C_3H_5O_3Na$,

the pH of the solution can be calculated from the Henderson-Hasselbalch Equation.

$$[C_3H_5O_3Na] = \frac{0.050\ mol \times 1000\ cm^3}{500\ cm^3} = 0.10\ mol\ dm^{-3}$$

$$[HC_3H_5O_3] = \frac{0.025\ mol \times 1000\ cm^3}{500\ cm^3} = 0.050\ mol\ dm^{-3}$$ *(0.5 point)*

$$pH = pK_a + \log([C_3H_5O_3Na] / [HC_3H_5O_3])$$ *(1 point)*

$$3.50 = pK_a + \log(0.050/0.10)$$

$$pK_a = 3.80$$ *(0.5 point)*

$$K_a = 1.58 \times 10^{-4}$$ *(0.5 point)*

The dissociation constant of lactic acid is …………1.58×10^{-4}…… *(0.5 point)*

Problem 5

5% of the total

Problem 5	A		B	C		D	Total
	A1	A2		C1	C2		
Total	1	1	3	1	2	2	10
Score							

Problem 5: Phosphate and silicate in soil

Distribution and mobility of phosphorus in soil are usually studied by sequential extraction. Sequential extraction is performed by the use of acid or alkaline reagents to fractionate inorganic phosphorus in soil. Soil sample was extracted and analyzed as follows:

Part A. Determination of total phosphate (PO_4^{3-}) and silicate (SiO_4^{4-})

A 5.00 gram of soil sample is digested to give a final volume of 50.0 cm^3 digesting solution which dissolves total phosphorus and silicon. The extract is analyzed for the total concentrations of phosphorus and silicon. The concentrations of phosphorus and silicon are found to be 5.16 mg dm^{-3} and 5.35 mg dm^{-3}, respectively.

5-A1) Determine the mass of PO_4^{3-} in mg per 1.00 g of soil.

Calculations

$\therefore$ 1 g of soil contains PO_4^{3-} = __________ mg (answer with 3 digits after decimal point)

5-A2) Determine the mass of SiO_4^{4-} in mg per 1.00 g of soil.

Calculations

$\therefore$ 1 g of soil contains SiO_4^{4-} = __________ mg (answer with 3 digits after decimal point)

Part B. Determination of available PO_4^{3-} in acid extract

Phosphate can be analyzed by using molybdenum blue method. One mole of phosphate is converted into one mole of molybdenum blue compound. This method is used for determination of phosphate in the acid extract. Absorbance (A) and transmittance (T) are recorded at 800 nm. The molar absorptivity of the molybdenum blue compound is 6720 dm^3 mol^{-1} cm^{-1} and all measurement is carried out in a 1.00-cm cuvette.

Transmittance and absorbance are given by the following equations:

$$T = I / I_o$$

$$A = \log (I_o / I)$$

where I is the intensity of the transmitted light and I_o is the intensity of the incident light.

5-B1) When the sample containing high concentration of phosphate is analyzed, a reference solution of 7.5×10^{-5} mol dm^{-3} of molybdenum blue compound is used for adjusting zero absorbance. The transmittance of the sample solution is then measured to be 0.55. Calculate the concentration of phosphate (mol dm^{-3}) in the sample solution.

Calculations

∴ concentration of phosphate in an unknown sample = ____________ mol dm^{-3}

Part C. Determination of PO_4^{3-} and SiO_4^{4-} in alkaline extract

Both phosphate and silicate ions can react with molybdate in alkaline solution, producing the yellow molybdophosphate and molybdatosilicate. Further reduction with ascorbic acid produces intense color molybdenum blue compounds. Both complexes exhibit maximum absorption at 800 nm. Addition of tartaric acid helps preventing interference from silicate in the determination of phosphate.

Two series of phosphate standard are treated with and without tartaric acid whereas a series of silicate standard is not treated with tartaric acid. Linear equations obtained from those calibration curves are as follows:

Conditions	Linear equations
Phosphate with and without tartaric acid	$y = 6720x_1$
Silicate without tartaric acid	$y = 868x_2$

y is absorbance at 800 nm,
x_1 is concentration of phosphate as mol dm^{-3},
x_2 is concentration of silicate as mol dm^{-3}

Absorbance at 800 nm of the alkaline fraction of the soil extract after treated with and without tartaric acid are 0.267 and 0.510, respectively.

5-C1) Calculate the phosphate concentration in the alkaline soil extract in mol dm^{-3} and calculate the corresponding phosphorous in mg dm^{-3}.

Calculations

$\therefore$ concentration of PO_4^{3-} = ______________ mol dm^{-3}

$\therefore$ concentration of P = ___________ mg dm^{-3}

(answer with 2 digits after decimal point)

5-C2) Calculate the silicate concentration from the soil sample in t the alkaline fraction in mol dm^{-3} and calculate the corresponding silicon in mg dm^{-3}.

Calculations

∴ concentration of SiO_4^{4-} = ____________ mol dm^{-3}

(answer with 2 digits after decimal point)

∴ concentration of Si = ____________ mg dm^{-3}

(answer with 2 digits after decimal point)

Part D. Preconcentration of ammonium phosphomolybdate

A 100 cm^3 of aqueous sample of ammonium phosphomolybdate ($(NH_4)_3PMo_{12}O_{40}$) compound is extracted with 5.0 cm^3 of an organic solvent. The organic-water partition coefficient (K_{ow}) is defined as the ratio of the concentration of the compound in the organic phase (c_o) to that in the water phase (c_w). K_{ow} of the ammonium phosphomolybdate is 5.0. The molar absorptivity of ammonium phosphomolybdate in the organic phase is 5000 dm^3 mol^{-1} cm^{-1}.

5-D) If the absorbance in the organic phase is 0.200, calculate the total mass of phosphorus (in mg unit) in the original aqueous sample solution. The optical pathlength of the cuvette is 1.00 cm.

Calculations

$\therefore$ total amount of P in the original aqueous solution = ____________ mg

Problem 5

5% of the total

Problem 5	A		B	C		D	Total
	A1	A2	B1	C1	C2	D1	
Total	1	1	3	1	2	2	10
Score							

Problem 5: Phosphate and silicate in soil

Distribution and mobility of phosphorus in soil are usually studied by sequential extraction. Sequential extraction is performed by the use of acid or alkaline reagents to fractionate inorganic phosphorus in soil. Soil sample was extracted and analyzed as follows:

Part A. Determination of total phosphate (PO_4^{3-}) and silicate (SiO_4^{4-})

A 5.00 gram of soil sample is digested to give a final volume of 50.0 cm^3 digesting solution which dissolves total phosphorus and silicon. The extract is analyzed for the total concentrations of phosphorus and silicon. The concentrations of phosphorus and silicon are found to be 5.16 mg dm^{-3} and 5.35 mg dm^{-3}, respectively.

5-A1) Determine the mass of PO_4^{3-} in mg per 1.00 g of soil. (1 point)

Calculations

P 30.97 g from PO_4^{3-} *94.97 g*

P 5.16 mg from PO_4^{3-} $(94.97/30.97) \times 5.16 = 15.82$ *mg* dm^{-3}

In 50 cm^3 *solution,* $PO_4^{3-} = (15.82/1000) \times 50 = 0.791$ *mg*

5 g of soil contains PO_4^{3-} *0.791 mg*

∴ 1 g of soil contains PO_4^{3-}= __*0.158*__ mg (answer in 3 digits after decimal point) *(1 point)*

5-A2) Determine the mass of SiO_4^{4-} in mg per 1.00 g of soil. (1 point)

Calculations

Si 28.09 g from SiO_4^{4-} *92.09 g*

Si 5.35 mg from SiO_4^{4-} $(92.09/28.09) \times 5.35 = 17.539$ *mg*

In 50 cm^3 *solution,* $SiO_4^{4-} = (17.539/1000)\times 50 = 0.877$ *mg*

5 g of soil contains SiO_4^{4-} *0.877 mg*

∴ 1 g of soil contains SiO_4^{4-}= __*0.175*__ mg (answer in 3 digits after decimal point) *(1 point)*

Part B. Determination of available PO_4^{3-} in acid extract

Phosphate can be analyzed by using molybdenum blue method. One mole of phosphate is converted into one mole of molybdenum blue compound. This method is used for determination of phosphate in the acid extract. Absorbance (A) and transmittance (T) are recorded at 800 nm. The molar absorptivity of the molybdenum blue compound is 6720 dm^3 mol^{-1} cm^{-1} and all measurement is carried out in a 1.00-cm cuvette.

Transmittance and absorbance are given by the following equations:

$$T = I / I_o$$

$$A = \log (I_o / I)$$

where I is the intensity of the transmitted light and I_o is the intensity of the incident light.

5-B1) When the sample containing high concentration of phosphate is analyzed, a reference solution of 7.5 x 10^{-5} mol dm^{-3} of molybdenum blue compound is used for adjusting zero absorbance. The transmittance of the sample solution is then measured to be 0.55. Calculate the concentration of phosphate (mol dm^{-3}) in the sample solution. (3 points)

Calculations *At a given wavelength* $A_{total} = A_1 + A_2$

$$-\log (T_{total}) = -\log(T_1) + -\log(T_2) = -\log(T_1T_2)$$

$T_1 = T_{solution\ for\ adjusting\ zero\ absorbance} = 10^{(-\varepsilon bC)}$

$= 10^{-(6720\ dm3mol\text{-}1cm\text{-}1)(1\ cm)(\ 7.5\ x\ 10\text{-}5\ mol\ dm\text{-}3)} = 10^{(-0.504)} = 0.3133$ (1 point)

$T_2 = T_{measured} = 0.55$

Method 1) $T_{sample} = T_{solution\ for\ adjusting\ zero\ absorbance}\ T_{measured}$

$= 0.313 \times 0.55 = 0.1723$ (1 point)

$-\log (T) = \varepsilon bC$

$C = -\log(0.1723) / (6720\ dm^3 mol^{-1} cm^{-1})(1\ cm)$

$= 1.136 \times 10^{-4}$ mol dm^{-3} (1 point)

Or Method 2) If $T = 0.313$, $A = -\log(T) = 0.504$

If $T = 0.55$, $A = -\log(T) = 0.2596$ (1 point)

$A_{sample} = A_{measured} + A_{solution\ for\ adjusting\ zero\ absorbance} = 0.2596 + 0.504 = 0.7636$ (1 point)

$C = 0.7636 / (6720\ dm^3\ mol^{-1} cm^{-1})(1\ cm) = 1.136 \times 10^{-4}$ mol dm^{-3} (1 point)

∴ concentration of an unknown sample = 1.14×10^{-4} mol dm^{-3}

Part C. Determination of PO_4^{3-} and SiO_4^{4-} in alkaline extract

Both phosphate and silicate ions can react with molybdate in alkaline solution, producing the yellow molybdophosphate and molybdatosilicate. Further reduction with ascorbic acid produces intense color molybdenum blue compounds. Both complexes exhibit maximum absorption at 800 nm. Addition of tartaric acid helps preventing interference from silicate in the determination of phosphate.

Two series of phosphate standard are treated with and without tartaric acid whereas a series of silicate standard is not treated with tartaric acid. Linear equations obtained from those calibration curves are as follows:

Conditions	Linear equations
Phosphate with and without tartaric acid	$y = 6720x_1$
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y is absorbance at 800 nm,
x_1 is concentration of phosphate as mol dm^{-3},
x_2 is concentration of silicate as mol dm^{-3}

Absorbance at 800 nm of the alkaline fraction of the soil extract after treated with and without tartaric acid are 0.267 and 0.510, respectively.

5-C1) Calculate the phosphate concentration in the alkaline soil extract in mol dm^{-3} and calculate the corresponding phosphorous in mg dm^{-3}. (1 point)

Calculations

Conc. $PO_4^{3-} = (0.267 / 6720) = 3.97 \times 10^{-5}$ *mol* dm^{-3}

∴ concentration of PO_4^{3-} = $\underline{\quad 3.97 \times 10^{-5} \quad}$ mol dm^{-3} *(0.5 point)*

Conc. $P = (3.97 \text{ x } 10^{-5} \text{mol dm}^{-3})(30.97 \text{ g mol}^{-1})(1000 \text{ mg g}^{-1}) = 1.23 \text{ mg dm}^{-3}$

∴ concentration of P = $\underline{\quad 1.23 \quad}$ mg dm^{-3} 2 digits after decimal point *(0.5 point)*

5-C2) Calculate the silicate concentration from the soil sample in t the alkaline fraction in mol dm^{-3} and calculate the corresponding silicon in mg dm^{-3}. (2 points)

Calculations

Abs of $PO_4^{3-} = (3.97 \times 10^{-5}\ mol\ dm^{-3})(6720) = 0.267$

Abs of $SiO_4^{4-}{}_{in\ sample} = 0.510 - 0.267 = 0.243$

Conc. $SiO_4^{4-} = (0.243 / 868) = 2.80 \times 10^{-4}\ mol\ dm^{-3}$

∴ concentration of SiO_4^{4-} = ___2.80×10^{-4}___ mol dm^{-3} *(1 point)*

Conc. $Si = (2.80 \times 10^{-4} mol\ dm^{-3})(28.09\ g\ mol^{-1})(1000\ mg\ g^{-1}) = 7.87\ mg\ dm^{-3}$

∴ concentration of Si = ___*7.87*___ mg dm^{-3} 2 digits after decimal point *(1 point)*

Part D. Preconcentration of ammonium phosphomolybdate

A 100 cm^3 of aqueous sample of ammonium phosphomolybdate ($(NH_4)_3PMo_{12}O_{40}$) compound is extracted with 5.0 cm^3 of an organic solvent. The organic-water partition coefficient (K_{ow}) is defined as the ratio of the concentration of the compound in the organic phase (c_o) to that in the water phase (c_w). K_{ow} of the ammonium phosphomolybdate is 5.0. The molar absorptivity of ammonium phosphomolybdate in the organic phase is 5000 $dm^3\ mol^{-1}\ cm^{-1}$.

5-D) If the absorbance in the organic phase is 0.200, calculate the total mass of phosphorus (in mg unit) in the original aqueous sample solution. The optical pathlength of the cuvette is 1.00 cm. (2 points)

Calculations

$C_o = 0.200/5000 = 4 \times 10^{-5}$ mol dm^{-3}

The volume of the organic phase is 5.0 cm^3, therefore ammonium phosphomolybdate in the organic phase

$= (4 \times 10^{-5}\ mol\ dm^{-3})(5\ cm^3) / 1000\ cm^3\ dm^{-3} = 2 \times 10^{-7}\ mol$ (0.5 point)

From $K_{ow} = C_o / C_w = 5.0$

$C_w = (4 \times 10^{-5}\ mol\ dm^{-3}) / 5 = 8 \times 10^{-6}\ mol\ dm^{-3}$ (0.5 point)

The volume of the aqueous solution is 100 cm^3, therefore ammonium phosphomolybdate in the aqueous solution

$= (8 \times 10^{-6}\ mol\ dm^{-3})(100\ cm^3) / 1000\ cm^3\ dm^{-3}$

$= 8 \times 10^{-7}\ mol$

Therefore, the total mol of ammonium phosphomolybdate $= (2 \times 10^{-7}) + (8 \times 10^{-7})$ mol

$= 1 \times 10^{-6}$ mol (0.5 point)

Total amount of P $= (1 \times 10^{-6}\ mol)(30.97\ g\ mol^{-1})(1000\ mg\ g^{-1}) = 0.031$ mg (0.5 point)

∴ total amount of P in the original aqueous solution = 0.031 mg

Theoretical Problem 4	Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	**Total**
	Points	2	5	1	2	7	2	3	2	**24**
6% of the total	Score									

Problem 4. Column chromatography of radioactive copper

^{64}Cu for positron emission tomography is prepared by the bombardment of a zinc target with deuterium nuclei (further referred to as the activated target).

4.1 Write down the balanced equation for the ^{64}Zn nucleus bombardment with deuterium nuclei, giving ^{64}Cu. Specify the corresponding atomic and mass numbers of all species. Disregard the charges of the species.

… $^{☐}_{☐}$☐ + … $^{☐}_{☐}$☐ → … $^{☐}_{☐}$☐ + … $^{☐}_{☐}$☐

The activated target is dissolved in concentrated hydrochloric acid (HCl (aq)) to give a mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes.

4.2 Calculate the mole fraction of negatively charged copper species with respect to the amount of copper prepared by zinc target activation. Assume [Cl$^-$] = 4 mol dm^{-3}. For the overall complexation constants, β, see Table 1.

Before you start the calculation, write down the charges in the upper right boxes:

Cu ☐ [CuCl]☐ [CuCl$_2$] ☐ [CuCl$_3$]☐ [CuCl$_4$] ☐

	i in [CuCl$_i$]			
	1	2	3	4
β_i	2.36	1.49	0.690	0.055

Table 1. Overall complexation constants β of Cu species (charges have been omitted in the formula).

$$\beta_i = \frac{[\mathrm{CuCl}_i]}{[\mathrm{Cu}]\cdot[\mathrm{Cl}]^i}\ .$$

Show your calculation:

Mole fraction =

(answer with 2 digits after decimal point)

The mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes was separated with an anion exchange resin. Dry resin in OH^- form was dispersed in water and the suspension was transferred into a column. To occupy all sites with Cl^- ions (i.e. to obtain resin in a Cl^- form), the resin was washed with hydrochloric acid and then with deionised water to wash out all the unbound Cl^- ions.

4.3 Everything was initially at laboratory temperature before washing with hydrochloric acid. Does the column temperature change during the washing with hydrochloric acid?

☐ No.

☐ Yes, the temperature decreases.

☐ Yes, the temperature increases.

The mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes was transferred onto the resin-filled column. Hydrochloric acid solution was used as an eluent.

Using the simple experimental formula below, you can calculate quantities that determine average elution properties of both copper species and zinc species on the column.

The retention volume V_R (the mobile phase volume at which 50% of the compound has been eluted from the column) can be calculated as follows:

$$\boldsymbol{V_R = D_g \times m_{\text{resin,dry,OH form}} + V_0}$$

4.4 Using the average mass distribution coefficients D_g (D_g(Cu species) = 17.4 $cm^3\ g^{-1}$, D_g(Zn species) = 78.5 $cm^3\ g^{-1}$), calculate the retention volume V_R in cm^3 of the copper species, and of the zinc species. The mass of dry resin in OH^- form $m_{\text{resin,dry,OH form}}$ = 3.72 g and the void volume of a column V_0 = 4.93 cm^3.

Show your calculation:

V_R(Cu species) = cm^3 (answer with 1 digit after the decimal point)

V_R(Zn species) = cm^3 (answer with 0 digit after the decimal point)

If you cannot find the answer, use V_R(Cu species) = 49.9 cm^3 and V_R(Zn species) = 324 cm^3 for further calculations.

Using this simple experimental formula, separation of two sets of species, **A** and **B**, can be considered complete if

$$\boldsymbol{V_{0.001}(\mathrm{A}) - V_{0.999}(\mathrm{B}) > 10V_c}$$

where $V_{0.001}$ is the mobile phase volume at which 0.1% of **A** has been eluted from the column, and $V_{0.999}$ is the mobile phase volume at which 99.9% of **B** has been eluted from the column.

$$\boldsymbol{V_{0.001}(\mathrm{A}) = V_R(\mathrm{A}) \times \left(1 - 6.91\sqrt{d_p/L_c}\right)}$$

$$\boldsymbol{V_{0.001}(\mathrm{B}) = V_R(\mathrm{B}) \times \left(1 - 6.91\sqrt{d_p/L_c}\right)}$$

$$\boldsymbol{V_{0.999}(\mathrm{B}) = 2V_R(\mathrm{B}) - V_{0.001}(\mathrm{B})}$$

4.5 Based on a calculation, decide whether copper species were separated completely from zinc species. The volume of the column filled with the swollen resin $V_c = 10.21$ cm^3, the resin particle diameter $d_p = 0.125$ mm, and the height of the wet resin in a swollen state in the column $L_c = 13.0$ cm.

$V_{0.001}(A) =$ cm^3

$V_{0.999}(B) =$ cm^3

It is possible to separate copper species from zinc species.

☐ True ☐ False

4.6 Calculate the theoretical value of the total ion exchange mass capacity of the dry resin used in this problem, $Q_{m,theor}$, in mmol g^{-1}. Assume that tetralkylammonium groups were the only ones responsible for ion exchange of the resin. No other nitrogen containing groups were present. The mass fraction of nitrogen in the dry resin was 4.83%.

$Q_{m,theor} =$ mmol g^{-1} (answer with 2 digits after decimal point)

If you cannot find the answer, use $Q_{m,theor} = 4.83$ mmol g^{-1} for further calculations.

In reality, not all tetraalkylammonium groups are involved in the ion exchange. To determine the total ion exchange volume capacity, Q_v, the column filled with 3.72 g dry resin converted to the Cl^- form was washed with the excess of sodium sulfate solution. The effluent was collected in a 500 cm^3 volumetric flask, which was then filled with water to the mark. An aliquot of 100 cm^3 was potentiometrically titrated with 0.1027 mol dm^{-3} silver nitrate. The silver nitrate solution volume at the equivalence point was 22.20 cm^3. The volume of the column filled with the swollen resin, V_c, was 10.21 cm^3.

4.7 Calculate the Q_v of the swollen resin in mmol of active tetraalkylammonium groups per cm^3 of the swollen resin.

Q_v = mmol cm^{-3} (answer with 2 digits after decimal point)

If you cannot find the answer, use Q_v = 1.00 mmol cm^{-3} for further calculations.

4.8 Calculate the mole fraction (x) of the tetraalkylammonium groups actively involved in the ion exchange.

x = (answer with 3 digits after decimal point)

Theoretical Problem 4 6% of the total	Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	**Total**
	Points	2	5	1	2	7	2	3	2	**24**
	Score									

Problem 4. Column chromatography of radioactive copper

^{64}Cu for positron emission tomography is prepared by the bombardment of a zinc target with deuterium nuclei (further referred to as the activated target).

4.1 Write down the balanced equation for the ^{64}Zn nucleus bombardment with deuterium nuclei, giving ^{64}Cu. Specify the corresponding atomic and mass numbers of all species. Disregard the charges.

$$\underset{\dots}{1}\ {}^{\boxed{64}}_{\boxed{30}}\boxed{\mathrm{Zn}} + \underset{\dots}{1}\ {}^{\boxed{2}}_{\boxed{1}}\boxed{\mathrm{H}} \rightarrow \underset{\dots}{1}\ {}^{\boxed{64}}_{\boxed{29}}\boxed{\mathrm{Cu}} + \underset{\dots}{2}\ {}^{\boxed{1}}_{\boxed{1}}\boxed{\mathrm{p}}$$

2 points (1 point if any mass number is missing or the reaction is written with a wrong stoichiometry; 0 points if both or other mistakes are made)

The activated target is dissolved in concentrated hydrochloric acid (HCl (aq)) to give a mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes.

4.2 Calculate the mole fraction of negatively charged copper species with respect to the amount of copper prepared by zinc target activation. Assume $[Cl^-] = 4$ mol dm^{-3}. For the overall complexation constants, β, see Table 1.

Before you start the calculation, write down the charges in the upper right boxes:

$$\mathrm{Cu}^{\boxed{2+}} \qquad [\mathrm{CuCl}]^{\boxed{+}} \qquad [\mathrm{CuCl_2}]^{\boxed{0}} \qquad [\mathrm{CuCl_3}]^{\boxed{-}} \qquad [\mathrm{CuCl_4}]^{\boxed{2-}}$$

1 point for correct charges for all species; 0 points for 1 or more incorrect charge(s)

Table 1. Overall complexation constants β of Cu species (charges were omitted in the formula).

$$\beta_i = \frac{[\mathrm{CuCl}_i]}{[\mathrm{Cu}] \times [\mathrm{Cl}]^i}$$

	i in $[\mathrm{CuCl}_i]$			
	1	2	3	4
β_i	2.36	1.49	0.690	0.055

Calculation:

The mole fraction is the sum of the distribution coefficients of $[CuCl_3]^-$ and $[CuCl_4]^{2-}$:

$([[CuCl_3]^-] + [[CuCl_4]^{2-}]) / c(Cu^{2+}) = (\beta_3 [Cl^-]^3 + \beta_4 [Cl^-]^4) / (1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 + \beta_3 [Cl^-]^3 + \beta_4 [Cl^-]^4) = (0.69 \times 4^3 + 0.055 \times 4^4) / (1 + 2.36 \times 4 + 1.49 \times 4^2 + 0.69 \times 4^3 + 0.055 \times 4^4) =$

$= 58.24 / 92.52 = 0.63$

Mole fraction: 0.63

(answer with 2 digits after decimal point)

4 points for completely correct answer; −1 point for the wrong mole fraction obtained by the correct procedure

The mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes was separated with an anion exchange resin. Dry resin in OH^- form was dispersed in water and the suspension was transferred into a column. To occupy all sites with Cl^- ions (i.e. to obtain resin in a Cl^- form), the resin was washed with hydrochloric acid and then with deionized water to wash out all the unbound Cl^- ions.

4.3 Everything was initially at laboratory temperature before washing with hydrochloric acid. Does the column temperature change during the washing with hydrochloric acid?

☐ No.

☐ Yes, the temperature decreases.

☒ Yes, the temperature increases.

1 point for the correct answer

The mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes was transferred onto the resin-filled column. Hydrochloric acid solution was used as an eluent.

Using the simple experimental formula below, you can calculate quantities that determine average elution properties of both copper species and zinc species on the column.

The retention volume V_R (the mobile phase volume at which 50% of the compound has been eluted from the column) can be calculated as follows:

$$\boldsymbol{V_R = D_g \times m_{resin,dry,OH\ form} + V_0}$$

4.4 Using the average mass distribution coefficients D_g (D_g(Cu species) = 17.4 $cm^3\ g^{-1}$, D_g(Zn species) = 78.5 $cm^3\ g^{-1}$), calculate the retention volumes V_R in cm^3 of both copper species and zinc species. The mass of dry resin in OH^- form $m_{resin,dry,OH\ form}$ = 3.72 g and the void volume of a column V_0 = 4.93 cm^3.

Calculation:

V_R(Cu species) = 69.7 cm^3 (answer with 1 digit after the decimal)

V_R(Zn species) = 297 cm^3 (answer with 0 digit after the decimal)

2 points in total (1 point for each V_R)

If you cannot find the answer, use V_R(Cu species) = 49.9 cm^3 and V_R(Zn species) = 324 cm^3 for further calculations.

Using the simple experimental formula, separation of two sets of species, **A** and **B**, can be considered complete if

$$V_{0.001}(\mathbf{A}) - V_{0.999}(\mathbf{B}) > 10V_c$$

where $V_{0.001}$ is the mobile phase volume at which 0.1% of **A** has been eluted from the column, and $V_{0.999}$ is the mobile phase volume at which 99.9% of **B** has been eluted from the column.

$$V_{0.001}(\mathbf{A}) = V_R(\mathbf{A}) \times \left(1 - 6.91\sqrt{d_p/L_c}\right)$$

$$V_{0.001}(\mathbf{B}) = V_R(\mathbf{B}) \times \left(1 - 6.91\sqrt{d_p/L_c}\right)$$

$$V_{0.999}(\mathbf{B}) = 2V_R(\mathbf{B}) - V_{0.001}(\mathbf{B})$$

4.5 Based on a calculation, decide whether copper species were separated completely from zinc species. The volume of the column filled with the swollen resin V_c = 10.21 cm^3, the resin particle diameter d_p = 0.125 mm, and the height of the wet resin in a swollen state in the column L_c = 13.0 cm.

According to the retention volumes (V_R), $V_{0.001}$(A) corresponds to $V_{0.001}$(Zn species) and $V_{0.999}$(B) corresponds to $V_{0.999}$(Cu species)

$V_{0.001}$(A) = 297 cm^3 × $(1 - 6.91 \times \sqrt{0.125\text{ mm}/130\text{ mm}})$ = 233 cm^3

2 points (1 point if L_c and d_p are used with different units;)

$V_{0.999}$(B) = 2 × 69.7 cm^3 − 54.8 cm^3 = 84.6 cm^3

1 point (even with the wrong V_R and $V_{0.001}$ for Cu species)

where $V_{0.001}$(Cu species) = 69.7 cm^3 × $(1 - 6.91 \times \sqrt{0.125\text{ mm}/130\text{ mm}})$ = 54.8 cm^3

2 points (1 point if L_c and d_p are used with different units)

It is possible to separate copper species from zinc species.

☒ True ☐ False

2 points for the correct decisions based on $V_{0.001}$ and $V_{0.999}$ calculations

4.6 Calculate the theoretical value of the total ion exchange mass capacity of the dry resin used in this problem, $Q_{\mathrm{m,theor}}$, in mmol $\mathrm{g^{-1}}$. Consider tetralkylammonium groups were the only ones responsible for ion exchange of the resin. No other nitrogen containing groups were present. The mass fraction of nitrogen in the dry resin was 4.83%.

$Q_{\mathrm{m,theor}} = w(\mathrm{N}) / M(\mathrm{N}) = 0.0483 / (14.01\ \mathrm{g\ mol^{-1}}) = 3.45\ \mathrm{mmol\ g^{-1}}$

2 points (1 point if the value is in the wrong order of magnitude)

(answer with 2 digits after decimal point)

If you cannot find the answer, use $Q_{\mathrm{m,theor}} = 4.83\ \mathrm{mmol\ g^{-1}}$ for further calculations.

In reality, not all tetraalkylammonium groups are involved in the ion exchange. To determine the total ion exchange volume capacity, Q_{v}, the column filled with 3.72 g dry resin converted to the $\mathrm{Cl^-}$ form was washed with the excess of sodium sulfate solution. The effluent was collected in a 500 $\mathrm{cm^3}$ volumetric flask, which was then filled with water to the mark. An aliquot of 100 $\mathrm{cm^3}$ was potentiometrically titrated with 0.1027 mol $\mathrm{dm^{-3}}$ silver nitrate. The silver nitrate solution volume at the equivalence point was 22.20 $\mathrm{cm^3}$. The volume of the column filled with the swollen resin, V_{c}, was 10.21 $\mathrm{cm^3}$.

4.7 Calculate the Q_{v} of the swollen resin in mmol of active tetraalkylammonium groups per $\mathrm{cm^3}$ of the swollen resin.

$Q_{\mathrm{v}} = V(\mathrm{AgNO_3}) \times c(\mathrm{AgNO_3}) \times V_{\mathrm{flask}} / (V_{\mathrm{aliquot}} \times V_{\mathrm{c}}) =$

$= 0.0222\ \mathrm{dm^3} \times 0.1027\ \mathrm{mol\ dm^{-3}} \times 0.500\ \mathrm{dm^3} / (0.100\ \mathrm{dm^3} \times 0.01021\ \mathrm{dm^3}) = 1.12\ \mathrm{mmol\ cm^{-3}}$

3 points
−1 point if dilution is forgotten
−1 point for the wrong order of magnitude
(1 point for titration calculation)

(answer with 2 digits after decimal point)

If you cannot find the answer, use $Q_{\mathrm{v}} = 1.00\ \mathrm{mmol\ cm^{-3}}$ for further calculations.

4.8 Calculate the mole fraction (x) of the tetraalkylammonium groups actively involved in the ion exchange.

$x = Q_{\mathrm{v}} \times V_c / (Q_{\mathrm{m,teor}} \times m_{\mathrm{resin}}) = 1.12\ \mathrm{mmol\ cm^{-3}} \times 10.21\ \mathrm{cm^3} / (3.45\ \mathrm{mmol\ g^{-1}} \times 3.72\ \mathrm{g}) = 0.891$

2 points

(answer with 3 digits after decimal point)

Sommario