THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/3C **CHEMISTRY 3C**

(For Both School and Private Candidates)

Time: 3 Hours **ANSWERS** **Year: 2013**

Instructions

1. This paper consists of THREE questions.

2. Answer all questions.

1. You are provided with the following:

T_3: A solution containing 0.65 g of impure potassium dichromate ($K_2Cr_2O_7$) in 0.10 dm^3 of distilled water

T_2: A solution made by dissolving 0.04 moles of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) in 0.4 dm^3 of distilled water

T_4: 10% potassium iodide solution

T_5: 1M sulphuric acid

T_6: Starch solution

Theory

Acidified potassium dichromate reacts quantitatively with potassium iodide solution liberating iodine according to the equation:

$Cr_2O_7^{2-} + 14H^+ + 6I^- \text{-----> } 2Cr^{3+} + 3I_2 + 7H_2O$ ...(1)

The liberated iodine can be titrated against sodium thiosulphate and the reaction taking place between iodine and thiosulphate can be represented by the equation:

$2S_2O_3^{2-} + I_2 \text{-----> } S_4O_6^{2-} + 2I^-$ ...(2)

Procedure

(i) Pipette 20 cm^3 or 25 cm^3 of solution T_1 into a clean conical flask

(ii) Add 20 cm^3 or 25 cm^3 of solution T_4 followed by 20 cm^3 or 25 cm^3 of solution T_3 and shake the mixture

(iii) Immediately titrate the mixture against solution T_2 from the burette until the solution becomes pale yellow

(iv) Add about 2 cm^3 of solution T_6 and continue titrating until a green colour appears

(v) Repeat procedures (i) to (iv) three times and record your data in a tabular form

Questions

(a) Calculate the concentration of T_2 in mol/dm^3

Moles of sodium thiosulphate = 0.04 mol

Volume = 0.4 dm^3

Concentration = 0.04 mol ÷ 0.4 dm^3 = 0.1 mol/dm^3

(b) Calculate the concentration of pure potassium dichromate in

(i) mol/dm^3

(ii) g/dm^3

Molar mass of $K_2Cr_2O_7$ = (2×39) + (2×52) + (7×16) = 294 g/mol

Mass = 0.65 g in 0.10 dm^3

Concentration in g/dm^3 = 0.65 ÷ 0.10 = 6.5 g/dm^3

Concentration in mol/dm^3 = 6.5 ÷ 294 = 0.0221 mol/dm^3

(c) Find the percentage purity of potassium dichromate

Let titre volume of T_2 = V cm^3

Moles of T_2 used = (0.1 × V)/1000

From equation (2), 1 mol of I_2 reacts with 2 mol of T_2

From equation (1), 1 mol of $Cr_2O_7^{2-}$ produces 1.5 mol of I_2

So, mole ratio: 1 mol $Cr_2O_7^{2-}$: 3 mol I_2 : 6 mol T_2

Moles of $Cr_2O_7^{2-}$ = (0.1 × V) / (1000 × 6) = V / 60000 mol

Mass = V / 60000 × 294 = (V × 294) ÷ 60000 g

Purity = [(V × 294) ÷ 60000] ÷ 0.065 × 100% = [(V × 294 × 100) ÷ (60000 × 0.65)]%

= (V × 2940000) ÷ 39000 ≈ 75.38V%

Actual purity depends on V from experimental results.

(d) Write down the half reactions for the reaction equations (1) and (2) above

Equation (1) half reactions:

Oxidation (I^- to I_2):

$2I^- \text{-----> } I_2 + 2e^-$

Reduction ($Cr_2O_7^{2-}$ to Cr^{3+}):

$Cr_2O_7^{2-} + 14H^+ + 6e^- \text{-----> } 2Cr^{3+} + 7H_2O$

Equation (2) half reaction:

$I_2 + 2e^- \text{-----> } 2I^-$

$2S_2O_3^{2-} \text{-----> } S_4O_6^{2-} + 2e^-$

2. You are provided with the following:

A_1: Distilled water

A_2: 4 g anhydrous copper (II) sulphate ($CuSO_4$)

A_3: 6 g copper (II) sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$)

Thermometer and Stirrer

Cotton wool

Procedure

(i) Take 100 ml beaker and put it into a 250 cm^3 beaker. Fill the space between using cotton wool as an insulator

(ii) Pour 50 cm^3 of A_1 into a 100 cm^3 beaker in (i)

(iii) Stir the water and record the temperature, T_1

(iv) Add A_2 into a beaker containing water. Stir gently until dissolution is complete

(v) Record the final temperature of the solution, T_2

(vi) Clean and dry the beaker, stirrer and thermometer. Then repeat steps (i) to (v) using A_3

(vii) Record your results in a tabular form as indicated in Table 1

Questions

(a) Find the temperature change $T = T_2 - T_1$ in each experiment

Let's assume from the experiment:

For A_2: $T_1 = 25°C$, $T_2 = 29.5°C \rightarrow \Delta T = 29.5 - 25 = +4.5°C$

For A_3: $T_1 = 25°C$, $T_2 = 21.3°C \rightarrow \Delta T = 21.3 - 25 = -3.7°C$

So,

Temperature change for $A_2 = +4.5°C$

Temperature change for $A_3 = -3.7°C$

(b) Calculate the enthalpy of solution of each salt, given that the specific heat of water is 4.18 $Jg^{-1}K^{-1}$ and the density of water is 1 g/cm^3

Heat change, $Q = mc\Delta T$

$m = 50$ g (since 50 cm^3 water, density = 1 g/cm^3), $c = 4.18\ Jg^{-1}K^{-1}$

For A_2:

$Q = 50 \times 4.18 \times 4.5 = 940.5$ J

Moles of $CuSO_4 = 4 \div 159.5 = 0.0251$ mol

$\Delta H = Q \div \text{moles} = 940.5 \div 0.0251 = +37475.3\ Jmol^{-1} = +37.48\ kJmol^{-1}$

For A_3:

$Q = 50 \times 4.18 \times (-3.7) = -772.3$ J

Moles of $CuSO_4 \cdot 5H_2O = 6 \div 249.5 = 0.02405$ mol

$\Delta H = -772.3 \div 0.02405 = -32118.1\ Jmol^{-1} = -32.12\ kJmol^{-1}$

(c) Accepted values for the two experiments are:

$\Delta H°soln\ (CuSO_4) = -66.10\ kJmol^{-1}$

$\Delta H°soln\ (CuSO_4 \cdot 5H_2O) = +11.30\ kJmol^{-1}$

How do the calculated enthalpies of each salt differ from the expected values? Give reasons.

For $CuSO_4$: Calculated $\Delta H = +37.48\ kJmol^{-1}$ vs accepted $= -66.10\ kJmol^{-1}$ → large difference and opposite sign.

For $CuSO_4 \cdot 5H_2O$: Calculated $\Delta H = -32.12\ kJmol^{-1}$ vs accepted $= +11.30\ kJmol^{-1}$ → large difference and opposite sign.

Reasons for differences:

- Heat losses to surroundings despite insulation

- Incomplete dissolution of salts

- Impurities in salts

- Inaccurate temperature readings due to rapid dissolution or evaporation

- Differences in molar mass used due to hydrated vs anhydrous forms not fully accounted

Hence, the calculated enthalpies deviate significantly due to experimental errors and heat exchange with surroundings.

3. You are provided with the following:

JJ: A solution of succinic acid in water

PP: 0.2 M sodium hydroxide

SS: Phenolphthalein indicator

OO: Diethyl ether

Theory

Ether and water are immiscible. When succinic acid is dissolved, it will distribute itself in the two liquids in such a way that

concentration of succinic acid in water / concentration of succinic acid in ether = constant.

In this experiment, you are required to determine the partition coefficient of succinic acid between water and diethyl ether at room temperature.

Procedure

Part 1

(i) Pipette 20 cm^3 or 25 cm^3 of JJ into a clean conical flask and add two drops of SS

(ii) Put PP into the burette and titrate it against JJ until colour change is observed. A single accurate titration is enough.

Summary:

___ cm^3 of solution JJ required ___ cm^3 of PP for complete reaction

Part 2

(i) Using a measuring cylinder measure 50 cm^3 of OO and transfer it into a separating funnel

(ii) Measure 50 cm^3 of JJ and transfer it into a separating funnel containing OO and then shake well. Leave the mixture to stand for about 3 minutes

(iii) Run the lower layer (aqueous layer) into a clean beaker. Measure 20 cm^3 or 25 cm^3 of the aqueous layer into a conical flask. Add to it two drops of SS

(iv) Put PP into a burette and titrate it against the aqueous layer in a conical flask until there is a colour change. Record the volume of PP used. A single accurate titration is enough.

Summary:

___ cm^3 of JJ required ___ cm^3 of PP for complete reaction

Questions

(a) The colour of the solution during titration changed from _____ to _____

The colour of the solution changed from colourless to pink.

This is due to phenolphthalein which is colourless in acid and pink in base, indicating the endpoint of the reaction.

(b) Write down the equation for the reaction between JJ and PP

Succinic acid ($H_2C_4H_4O_4$) reacts with sodium hydroxide as follows:

$H_2C_4H_4O_4 + 2NaOH$ -----> $Na_2C_4H_4O_4 + 2H_2O$

This shows a dibasic acid neutralised by two moles of base.

(c)(i) Calculate the concentration of JJ before it was mixed with OO in g/dm^3

Let's say from titration before mixing:

25 cm^3 of JJ required 20.0 cm^3 of 0.2 M NaOH

Moles of NaOH = (0.2 × 20.0)/1000 = 0.004 mol

Since 2 mol NaOH reacts with 1 mol succinic acid:

Moles of succinic acid = 0.004 ÷ 2 = 0.002 mol in 25 cm^3

Concentration in mol/dm^3 = (0.002 × 1000)/25 = 0.08 mol/dm^3

Molar mass of succinic acid = 118 g/mol

Concentration in g/dm^3 = 0.08 × 118 = 9.44 g/dm^3

(ii) Calculate the concentration of JJ in water after mixing with OO in g/dm^3

Suppose after mixing, 25 cm^3 of aqueous layer required 10.0 cm^3 of 0.2 M NaOH

Moles of NaOH = (0.2 × 10.0)/1000 = 0.002 mol

Moles of succinic acid = 0.002 ÷ 2 = 0.001 mol

Concentration in mol/dm^3 = (0.001 × 1000)/25 = 0.04 mol/dm^3

Concentration in g/dm^3 = 0.04 × 118 = 4.72 g/dm^3

(iii) Calculate the concentration of JJ in ether in g/dm^3

Original concentration = 9.44 g/dm^3

Aqueous concentration after extraction = 4.72 g/dm^3

Amount transferred to ether = 9.44 − 4.72 = 4.72 g

Volume of ether = 50 cm^3 = 0.05 dm^3

Concentration in ether = 4.72 ÷ 0.05 = 94.4 g/dm^3

(iv) Partition coefficient of succinic acid between water and ether at the temperature of the experiment

K = concentration in water / concentration in ether = 4.72 ÷ 94.4 = 0.05

4. Substance M contains a common cation and two anions. Use the information given in the experiment column in Table 2 to complete the observations and inferences and hence identify the common cation and the two anions.

S/n	Experiment	Observations	Inferences		
1	Appearance	White crystalline solid	Possible presence of chloride or sulphate		
2	Perform flame test	Yellow flame	Presence of Na^+ ion		
3	To a little sample M	add Conc. H_2SO_4 and warm gently	Colourless gas with pungent smell evolved	turns blue litmus red	Presence of Cl^- ion (HCl evolved)
4(i)	Add $AgNO_3$ solution to first portion	White ppt formed	soluble in NH_3	Confirms Cl^- ion	
4(ii)	Add fresh $FeSO_4$ and conc. H_2SO_4 slowly	Brown ring formed at the junction	Presence of NO_3^- ion		
4(iii)	Add $BaCl_2$ solution	No ppt	Absence of SO_4^{2-}		
4(iv)	Add aqueous ammonia till excess	No ppt	Confirms Na^+ as cation (Group I	no ppt with NH_3) |	
5	Perform two confirmatory tests	Confirmations for Na^+ (yellow flame)	Cl^- (white ppt with $AgNO_3$)	NO_3^- (brown ring)	Valid

Conclusion

The cation in the sample M is Na^+ and the anions are Cl^- and NO_3^-.