THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/3A CHEMISTRY 3A

(For Both School and Private Candidates)

Time: 3 Hours ANSWERS Year: 2011

Instructions

- 1. This paper consists of THREE questions.
- 2. Answer all questions.



1. You are provided with the following solutions:
KO: Solution containing 3.35 g of pure sodium oxalate in 0.50 dm³ of solution
DM: Solution containing 3.20 g of impure potassium permanganate in 1 dm³ of solution
GS: 3M sulphuric acid
Theory
An acidified oxalate solution warmed at $70^{\circ}\text{C}-80^{\circ}\text{C}$ is titrated against permanganate solution. From the titration results, the purity of the potassium permanganate can be calculated.
Balanced equation:
$5C_2O_4^{2-} + 2MnO_4^{-} + 16H^{+}> 2Mn^{2+} + 10CO_2 + 8H_2O$
Procedure
(i) Pipette 25 cm³ or 20 cm³ of solution KO into a 250 cm³ titration flask
(ii) Add 60 cm ³ of solution GS
(iii) Heat the mixture to about 80°C
(iv) Titrate the hot solution with the permanganate solution DM until complete colour change is observed
(v) Repeat titration and record all results
Summary:
cm³ of solution KO require cm³ of solution DM for completion of the reaction
Ouestions

(a) Calculate the concentration of KO in moles per litre (dm³)

Molar mass of $Na_2C_2O_4 = 134 \text{ g/mol}$

Moles =
$$3.35 \div 134 = 0.025$$
 mol

Volume =
$$0.50 \text{ dm}^3$$

Concentration =
$$0.025 \div 0.5 = 0.05 \text{ mol/dm}^3$$

(b)(i) Calculate the concentration of solution DM in moles per litre

Molar mass of
$$KMnO_4 = 158 \text{ g/mol}$$

Moles =
$$3.20 \div 158 = 0.02025$$
 mol

Volume =
$$1 \text{ dm}^3$$

Concentration =
$$0.02025 \text{ mol/dm}^3$$

- (ii) Concentration in $g/dm^3 = 3.20 g/dm^3$
- (c) Calculate the percentage purity of potassium permanganate

Suppose average titre = 25.0 cm³ of DM required for 25.0 cm³ of KO

Moles of oxalate =
$$25.0 \div 1000 \times 0.05 = 0.00125$$
 mol

From balanced equation:

$$5C_2O_4^{2-}: 2MnO_4^{-} \rightarrow 5:2 \text{ mol ratio}$$

Moles of KMnO₄ =
$$(0.00125 \times 2)/5 = 0.0005$$
 mol

Mass =
$$0.0005 \times 158 = 0.079$$
 g

Volume of DM =
$$25.0 \text{ cm}^3 = 0.025 \text{ dm}^3$$

Mass per dm³ =
$$0.079 \times (1000 \div 25) = 3.16 \text{ g/dm}^3$$

Purity =
$$(3.16 \div 3.20) \times 100 = 98.75\%$$

(d) Give the half reaction equations and indicate which species are oxidized or reduced

Oxidation ($C_2O_4^{2-}$ to CO_2):

$$C_2O_4^{2-}$$
 ----> $2CO_2 + 2e^-$

Reduction (MnO₄⁻ to Mn²⁺):

$$MnO_4^- + 8H^+ + 5e^- - Mn^{2+} + 4H_2O$$

 $C_2O_4^{2-}$ is oxidized, MnO_4^- is reduced.

2. You are provided with the following:

PQ: 1.6 g of anhydrous copper sulphate

MQ: 2.5 g of hydrated copper sulphate (CuSO₄·5H₂O)

Procedure

- (a) Set up the apparatus as shown
- (b) Pour 50 cm³ of distilled water into the polystyrene cup and measure its temperature
- (c) Tip the solid PQ into water and stir gently until complete dissolution
- (d) Record the maximum temperature
- (e) Repeat using MQ

Results:

Let's assume:

Initial temperature = 25° C

Final temp with PQ = $30.4^{\circ}\text{C} \rightarrow \Delta T = +5.4^{\circ}\text{C}$

Final temp with MQ = 21.8° C $\rightarrow \Delta$ T = -3.2° C

Questions

- (a) Calculate the enthalpy of solution of the two forms of the salt
- (i) PQ

Moles =
$$1.6 \div 159.5 = 0.01003$$
 mol

$$Q = mc\Delta T = 50 \times 4.2 \times 5.4 = 1134 J$$

$$\Delta H = 1134 \div 0.01003 = 113037 \text{ J/mol} = +113.04 \text{ kJ/mol}$$

(ii) MQ

Moles =
$$2.5 \div 249.5 = 0.01002$$
 mol

$$Q = 50 \times 4.2 \times (-3.2) = -672 \text{ J}$$

$$\Delta H = -672 \div 0.01002 = -67066.87 \text{ J/mol} = -67.07 \text{ kJ/mol}$$

- (b) Explain the difference in the values of enthalpy of solution obtained for the two forms of the salt
- PQ is anhydrous, so it releases energy when it hydrates in water (exothermic), resulting in a higher enthalpy change.

MQ is already hydrated, so its dissolution absorbs energy to break the hydration shell (endothermic), giving a negative enthalpy.

Thus, the difference is due to the hydration energy already present in MQ but absent in PQ.

3. You are provided with the following:

W₁: 0.1 M sodium hydroxide

W₂: Solution of succinic acid

W₃: Phenolphthalein indicator

W4: Diethyl ether

Theory

At constant temperature succinic acid dissolves in both water and diethyl ether while maintaining a constant ratio of concentration in solvents under consideration.

Procedure 1

- (i) Pipette 25 cm³ or 20 cm³ of W2 into a clean conical flask. Add to it 2-3 drops of W3
- (ii) Put W₁ into the burette
- (iii) Titrate very carefully solution W_2 against W_1 till there is a colour change. Record the volume of W_1 used.
- (a) Results
- (i) The volume of pipette used was ____ cm³
- (ii) Volume of W₁ used was cm³

Procedure 2

- (i) Measure 100 cm³ of W₄ using a measuring cylinder and place it into a separating funnel
- (ii) Add 100 cm³ of W₂ by means of measuring cylinder into the funnel in (i) above, shake well and allow the system to stand for a few minutes
- (iii) Run off the aqueous layer into a clean beaker. Using measuring cylinder put 25 cm³ of the aqueous layer into a clean conical flask. Titrate very carefully this aliquot against W₁ using W₃ as an indicator. Record the volume of W₁ used.
- (b) Results
- (i) Volume of aqueous layer taken was ____ cm³
- (ii) Volume of W₁ used was ____ cm³
- (c) Write a balanced chemical equation representing the reaction taking place in procedures (1) and (2) above

 $HOOC-CH_2CH_2-COOH + 2NaOH -----> NaOOC-CH_2CH_2-COONa + 2H_2O$

Succinic acid reacts with two moles of sodium hydroxide in neutralization.

- (d) Calculate the following:
- (i) Initial concentration of W2 in water before mixing

Let volume of W_2 used = 25 cm³

Volume of W_1 used = 20 cm^3

Concentration of $W_1 = 0.1 \text{ mol/dm}^3$

Moles of NaOH = $(0.1 \times 20)/1000 = 0.002$ mol

Since 2 mol NaOH react with 1 mol succinic acid:

Moles of succinic acid = $0.002 \div 2 = 0.001$ mol

Concentration of $W_2 = (0.001 \times 1000) \div 25 = 0.04 \text{ mol/dm}^3$

Molar mass = 118 g/mol

Concentration in $g/dm^3 = 0.04 \times 118 = 4.72 \text{ g/dm}^3$

(ii) Final concentration of W2 in the aqueous layer

Suppose 25 cm³ of aqueous layer required 10 cm³ of W₁

Moles of NaOH = $(0.1 \times 10)/1000 = 0.001$ mol

Moles of succinic acid = $0.001 \div 2 = 0.0005$ mol

Concentration = $(0.0005 \times 1000)/25 = 0.02 \text{ mol/dm}^3$

Concentration in $g/dm^3 = 0.02 \times 118 = 2.36 g/dm^3$

(e) Deduce the concentration of W₂ in the organic layer

Total acid before mixing = 4.72 g

Aqueous concentration after = 2.36 g

Acid in organic = 4.72 - 2.36 = 2.36 g

Volume of ether = $100 \text{ cm}^3 = 0.1 \text{ dm}^3$

Concentration = $2.36 \div 0.1 = 23.6 \text{ g/dm}^3$

(f) Calculate the partition coefficient of W2 between water and diethyl ether W4

 $K_d = concentration in aqueous / concentration in ether$

$$K_d = 2.36 \div 23.6 = 0.1$$

This means succinic acid is ten times more soluble in ether than in water under the given conditions.