THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 CHEMISTRY 2

Time: 3 Hours ANSWERS Mwaka: 2018

Instructions

- 1. This paper consists of a total of six questions
- 2. Answer five questions.



1 (a) Define the following:

(i) Rate of reaction

The rate of reaction is the change in concentration of a reactant or product per unit time.

(ii) Rate constant

Rate constant (k) is a proportionality constant in the rate equation which is specific for a particular reaction at a given temperature.

(iii) Reaction mechanism

Reaction mechanism is the step-by-step sequence of elementary reactions by which an overall chemical change occurs.

(iv) Molecularity of reaction

Molecularity is the number of reacting species (atoms, ions, molecules) involved in an elementary reaction step.

(v) Zero order reaction

A reaction in which the rate is independent of the concentration of the reactant.

(vi) Half-life

Half-life is the time required for the concentration of a reactant to reduce to half its initial value.

$$2NO(g) + 2H_2(g) ----> N_2(g) + 2H_2O(g)$$

Experiment | [NO] | [H₂] | Initial rate

$$1 \mid 5 \times 10^{-3} \mid 2 \times 10^{-3} \mid 1.3 \times 10^{-5}$$

$$2 \mid 10 \times 10^{-3} \mid 2 \times 10^{-3} \mid 5 \times 10^{-5}$$

$$3 \mid 10 \times 10^{-3} \mid 4 \times 10^{-3} \mid 1 \times 10^{-4}$$

(i) Determine the order with respect to each reactant and the overall order.

Comparing experiment 1 and 2: [NO] doubles, rate increases 4 times. So order with respect to NO is 2.

Comparing experiment 2 and 3: [H₂] doubles, rate doubles. So order with respect to H₂ is 1.

Overall order =
$$2 + 1 = 3$$

(ii) Establish the rate law for the reaction.

Rate =
$$k[NO]^2[H_2]$$

(iii) Calculate the rate constant.

Using experiment 1:

$$1.3 \times 10^{-5} = k \times (5 \times 10^{-3})^2 \times (2 \times 10^{-3})$$

$$1.3 \times 10^{-5} = k \times 5 \times 10^{-8}$$

$$k = 1.3 \times 10^{-5} / 5 \times 10^{-8} = 260 \text{ s}^{-1} \cdot \text{M}^{-2}$$

- 1 (c) Conversion of cyclopropane to propene is first order, rate constant $k = 6.7 \times 10^{-4} \text{ s}^{-1}$
- (i) [A]₀ = 0.25 M, t = 8.8 min = 528 sec [A] = [A]₀e[^](-kt) = 0.25e[^](-6.7×10⁻⁴ × 528) = 0.25e[^](-0.354) $\approx 0.25 \times 0.702 \approx 0.176$ M
- (ii) Time for [A] to decrease from 0.25 M to 0.15 M:

$$\ln([A]_0/[A]) = kt \to \ln(0.25/0.15) = 6.7 \times 10^{-4} \times t$$

$$t = ln(1.667)/6.7 \times 10^{-4} = 0.511/6.7 \times 10^{-4} \approx 763 \text{ sec} \approx 12.7 \text{ min}$$

(iii) Time for 74% conversion \rightarrow 26% remaining = 0.25×0.26 = 0.065 M ln(0.25/0.065) = 6.7×10⁻⁴ × t t = ln(3.846)/6.7×10⁻⁴ = 1.35/6.7×10⁻⁴ ≈ 2015 sec ≈ 33.6 min

2 (a)

(i) Briefly explain the term oxidation—reduction reaction.

It is a chemical reaction in which electrons are transferred between species, involving oxidation (loss of electrons) and reduction (gain of electrons).

(ii) Reaction:
$$Cr_2O_7^{2-} + Cl^- ---- > Cr^{3+} + Cl_2$$

Half equations:

Oxidation: $2Cl^{-} ----> Cl_{2} + 2e^{-}$

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

Balanced redox equation:

$$Cr_2O_7^{2-} + 14H^+ + 6Cl^- ----> 2Cr^{3+} + 7H_2O + 3Cl_2$$

2 (b) State which of the following are oxidation-reduction reactions:

(i)
$$CH_4(g) + 2O_2(g) ----> CO_2(g) + 2H_2O(g)$$

This is an oxidation-reduction (redox) reaction. Carbon in CH₄ is oxidized (from -4 to +4 in CO₂), and oxygen is reduced (from 0 to -2 in H₂O).

(ii)
$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

This is a redox reaction. Zinc is oxidized from 0 to +2 and hydrogen ions in HCl are reduced from +1 to 0 in H₂.

(iii)
$$Cr_2O_7^{2-}(aq) + 2OH^{-}(aq) ----> 2CrO_4^{2-}(aq) + H_2O(1)$$

This is a redox reaction. Chromium changes oxidation state from +6 in $Cr_2O_7^{2-}$ to +6 in CrO_4^{2-} , but this change is not redox in terms of electron transfer — it is a rearrangement in oxidation states within the same element and usually referred to as an acid-base reaction in alkaline medium.

(iv)
$$O_3(g) + NO(g) ----> O_2(g) + NO_2(g)$$

This is a redox reaction. NO is oxidized (N from +2 to +4), and O₃ is reduced (O from 0 to -2 in O₂).

Therefore:

- (i) **✓** Redox reaction
- (ii) ✓ Redox reaction
- (iii) **X** Not a redox reaction in conventional electron-transfer terms
- (iv) ✓ Redox reaction
- 2 (c) Identify oxidizing and reducing agents, oxidized and reduced species in 2(b):
- (i) Oxidizing agent: O₂, Reducing agent: CH₄ CH₄ oxidized to CO₂, O₂ reduced to H₂O
- (ii) Oxidizing agent: HCl, Reducing agent: Zn Zn oxidized to Zn^{2+} , H^+ reduced to H_2
- (iii) Oxidizing agent: Cr₂O₇²⁻, Reducing agent: OH⁻ OH⁻ oxidized to H₂O, Cr reduced to CrO₄²⁻
- (iv) Oxidizing agent: O₃, Reducing agent: NO NO oxidized to NO₂, O₃ reduced to O₂
- 2 (d) Calculate e.m.f of cell: $Pb(s)/Pb^{2+}(1\times10^{-3} M)/Cu^{2+}(1\times10^{-2} M)/Cu(s)$

$$\begin{split} E^{o}\text{cell} &= E^{o}(Cu) - E^{o}(Pb) = 0.34 - (-0.126) = 0.466 \text{ V} \\ \text{Ecell} &= E^{o}\text{cell} - (0.059/n) \log([Pb^{2+}]/[Cu^{2+}]) \\ \text{Ecell} &= 0.466 - (0.059/2) \log(10^{-3}/10^{-2}) \\ \text{Ecell} &= 0.466 - 0.0295 \times \log(0.1) = 0.466 - 0.0295 \times (-1) = 0.4955 \text{ V} \end{split}$$

- 3 (a) Define the following:
- (i) Conjugate base

A conjugate base is the species formed when an acid donates a proton (H⁺). Example: Cl⁻ is the conjugate base of HCl.

(ii) Conjugate acid

A conjugate acid is the species formed when a base accepts a proton (H⁺). Example: NH₄⁺ is the conjugate acid of NH₃.

(iii) Conjugate acid-base pair

These are two species that differ by one proton (H⁺), where one is the acid and the other is its conjugate base or vice versa.

Example: H₂O and OH⁻

3 (b) Identify the acid, base and acid-base conjugates for each of the following equations:

(i) $H_2O + HCl ----> H_3O^+ + Cl^-$

Acid: HCl Base: H₂O

Conjugate acid: H₃O⁺ Conjugate base: Cl⁻

(ii) $CH_3COOH + H_2O ----> H_3O^+ + CH_3COO^-$

Acid: CH₃COOH

Base: H₂O

Conjugate acid: H₃O⁺ Conjugate base: CH₃COO⁻

(iii) $CH_3COOH + H_2SO_4 ----> CH_3COOH_2^+ + HSO_4^-$

Acid: H₂SO₄ Base: CH₃COOH

Conjugate acid: CH₃COOH₂⁺ Conjugate base: HSO₄⁻

(iv) $C_6H_5NH_2 + NH_3 ----> C_6H_5NH^- + NH_3^+$

Acid: C₆H₅NH₂ Base: NH₃

Conjugate acid: NH₄⁺ Conjugate base: C₆H₅NH⁻

3 (c) Calculate the concentration of sodium propanoate (CH₃CH₂COONa) that must be present in a 0.01 M solution of propanoic acid (CH₃CH₂COOH) to produce a pH of 4.30 if Ka for propanoic acid is 1.3×10⁻⁵.

Using Henderson-Hasselbalch equation:

$$\begin{split} pH &= pKa + log([salt]/[acid]) \\ 4.30 &= -log(1.3 \times 10^{-5}) + log([salt]/0.01) \\ 4.30 &= 4.89 + log([salt]/0.01) \\ log([salt]/0.01) &= 4.30 - 4.89 = -0.59 \\ [salt]/0.01 &= 10^{-0.59} \approx 0.257 \\ [salt] &= 0.00257 \ M \end{split}$$

3 (d) Calculate the pH of 0.02 M acetic acid (CH₃COOH). The dissociation constant (Ka) of acetic acid is 1.8×10⁻⁵.

Ka =
$$[H^+]^2$$
 / [acid]
 $[H^+]^2$ = Ka × [acid] = $1.8 \times 10^{-5} \times 0.02 = 3.6 \times 10^{-7}$
 $[H^+] = \sqrt{3.6 \times 10^{-7}} = 6 \times 10^{-4} \text{ M}$
pH = $-\log(6 \times 10^{-4}) = 3.22$

- 4 (a) Write the solubility product constant (Ksp) expressions for the solubility equilibria of each of the following compounds:
- (i) Copper(I) bromide: $CuBr \rightleftharpoons Cu^+ + Br^ Ksp = [Cu^+][Br^-]$
- (ii) Bismuth sulphide: $Bi_2S_3 \rightleftharpoons 2Bi^{3+} + 3S^{2-}$ $Ksp = [Bi^{3+}]^2[S^{2-}]^3$
- (iii) Copper(I) iodate: $Cu(IO_3) \rightleftharpoons Cu^+ + IO_3^ Ksp = [Cu^+][IO_3^-]$
- (iv) Silver chromate: $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$ $Ksp = [Ag^+]^2[CrO_4^{2-}]$
- 4 (b) The [Ag⁺] of a solution is 4×10^{-3} . Calculate the [Cl⁻] that must be exceeded before AgCl can precipitate. The Ksp of AgCl is 1.0×10^{-10} .

$$\begin{split} Ksp &= [Ag^+][Cl^-] \\ 1.0 \times 10^{-10} &= 4 \times 10^{-3} \times [Cl^-] \\ [Cl^-] &= 1.0 \times 10^{-10} \ / \ 4 \times 10^{-3} = 2.5 \times 10^{-8} \ M \end{split}$$

4 (c) 25 cm³ of 0.001 M BaCl₂ solution were mixed with 40 cm³ of 0.002 M Na₂SO₄ solution. Will BaSO₄ precipitate from this solution?

Moles of Ba²⁺ =
$$0.001 \times 25/1000 = 2.5 \times 10^{-5}$$

New concentration after mixing = 2.5×10^{-5} / (25+40)mL = 2.5×10^{-5} / 65×10^{-3} = 3.85×10^{-4} M

Moles of
$$SO_4^{2-} = 0.002 \times 40/1000 = 8 \times 10^{-5}$$

New $[SO_4^{2-}] = 8 \times 10^{-5} / 65 \times 10^{-3} = 1.23 \times 10^{-3}$ M

Q =
$$[Ba^{2+}][SO_4^{2-}] = 3.85 \times 10^{-4} \times 1.23 \times 10^{-3} = 4.74 \times 10^{-7}$$

Since Q > Ksp (1.12×10⁻¹⁰), BaSO₄ will precipitate.

4 (d) (i) Outline four factors which affect the solubility of sparingly soluble salts:

Common ion effect

Temperature

pH of the solution

Presence of complexing agents

(ii) Calculate the solubility of AgCl in 0.20 M AgNO₃.

$$Ksp = [Ag^+][Cl^-]$$

 $[Ag^+] = 0.20 M$

$$1 \times 10^{-10} = 0.20 \times [Cl^{-}] ---> [Cl^{-}] = 5 \times 10^{-10} \text{ M}$$

5. (a) Why hydrogen element was placed in group I in the modern periodic table?

Hydrogen has one electron in its outermost shell-like alkali metals in group I and forms H⁺ ion by losing that electron, similar to alkali metals.

- 5 (b) Account for the following:
- (i) The cationic size of an element is smaller than its atomic size.

When an atom loses electrons to form a cation, the remaining electrons experience a stronger electrostatic pull from the nucleus, hence the cation becomes smaller.

(ii) Group I elements are called alkaline metals.

Group I elements form alkaline solutions (hydroxides) when they react with water, hence they are known as alkali metals.

(iii) Group II elements melt at higher temperatures than group I elements.

Group II elements have stronger metallic bonds due to smaller atomic radii and more delocalized electrons per atom, leading to higher melting points.

(iv) Some compounds are said to be polarized.

A compound is said to be polarized if there is an uneven distribution of electron density between bonded atoms, resulting in partial charges due to differences in electronegativity.

- 5 (c) Briefly explain the following facts:
- (i) Every first member of the group in the periodic table behaves anomalously from other members. First members like Li, Be, B, C etc. have small size, high ionization energy, and high electronegativity, leading to differences in behavior compared to others in the group.
- (ii) Some elements in the periodic table show diagonal relationships.

Certain elements (e.g., Li with Mg, Be with Al) show similarities in properties due to similar size and charge density, known as diagonal relationships.

(iii) Some elements are called d-block elements.

d-block elements are those whose last electron enters the d-orbital. They are transition metals in groups 3–12.

(iv) The compounds of Sc³⁺ are colourless.

Sc³⁺ has no electrons in its d-orbital (d⁰ configuration), so no d-d transitions occur, hence its compounds are colourless.

- 5 (d) The valency shell electronic configuration of element X is represented as 6s²6p¹.
- (i) Give the block, group and period of element X in the periodic table.

Block: p-block Group: Group 13 Period: Period 6

- (ii) Give the possible oxidation state of element X.
- +3 and +1 (common for group 13 elements)
- (iii) Give the formula of the oxide of X.

 X_2O_3 (if oxidation state is +3)

6 (a) Briefly describe the extraction process of tin from its chief ore.

Tin is extracted from its ore cassiterite (SnO₂) using the following steps:

- 1. Crushing and concentration by gravity separation.
- 2. Roasting to remove impurities like sulphur and arsenic.
- 3. Reduction using carbon: $SnO_2 + C \longrightarrow Sn + CO_2$
- 4. Purification by liquation or electrolytic refining.
- 6 (b) Briefly describe the chemical extraction of aluminum from its chief ore.
- 1. Ore: Bauxite (Al₂O₃·2H₂O)
- 2. Purification: Bayer's process dissolving bauxite in NaOH, filtering out impurities, and precipitating pure Al(OH)₃
- 3. Electrolysis: Hall-Heroult process Electrolysis of Al₂O₃ dissolved in molten cryolite.

Cathode: $Al^{3+} + 3e^{-} ----> Al$ Anode: $C + O^{2-} ----> CO_2$

7 (a) (i) Classify the following oxides:

Al₂O₃ – Amphoteric

Na₂O – Basic

ZnO – Amphoteric

CaO – Basic

(ii) Uses of sulphates of selected metals in different fields:

MgSO₄ – used in medicine (Epsom salt)

FeSO₄ – used in fertilizers

CuSO₄ – used as fungicide

Al₂(SO₄)₃ – used in water purification

BaSO₄ – used in radiology as contrast medium

- 7 (b) Explain these facts with suitable equations:
- (i) The aqueous solution of iron (III) chloride is acidic.

$$FeCl_3 + 3H_2O ----> Fe(OH)_3 + 3HCl$$

(ii) Gaseous iron (III) chloride at low temperature exists as a dimer and is a covalent compound.

(iii) Red hot iron decomposes steam reversibly.

$$3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$$

(iv) The aqueous solution of sodium hydrogen carbonate is alkaline.

$$NaHCO_3 + H_2O \rightleftharpoons Na^+ + OH^- + H_2CO_3$$

7 (c) Why iron (III) carbonate does not exist?

Fe³⁺ ion is small and highly charged, polarizing the large CO₃²⁻ ion, leading to decomposition into Fe(OH)₃ and CO₂ in water.

7 (d) With suitable examples, describe the chemistry of zinc oxide (ZnO).

ZnO is amphoteric.

With acids: ZnO + 2HCl ----> ZnCl₂ + H₂O

With bases: ZnO + 2NaOH + H₂O ----> Na₂[Zn(OH)₄]

8 (a) Outline any six control measures which are useful in minimizing the chemical pollution of water bodies.

Proper waste treatment

Use of biodegradable substances

Reducing use of chemical fertilizers

Proper disposal of industrial effluents

Legislation and regulation enforcement

Public awareness campaigns

8 (b) Outline any four possible causes of environmental degradation.

Deforestation

Industrial pollution

Overgrazing

Urbanization and poor waste disposal

8 (c) Briefly explain eight effects of air pollution to living organisms.

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Respiratory diseases
Irritation of eyes and skin
Reduction in crop yield
Acid rain effect
Damage to wildlife
Ozone layer depletion
Neurological disorders
Premature death in sensitive individuals

9 (a) Arrange the following amines in order of increasing basic strength:

Aniline < N-methylaniline < Benzylamine < Ethylamine

Reason: Aniline's lone pair delocalizes into benzene ring reducing availability for protonation. Alkyl groups increase electron density on nitrogen enhancing basicity.

- 9 (b) How n-propylamine could be prepared from each compound:
- (i) n-Propylbromide: CH₃CH₂CH₂Br + NH₃ ----> CH₃CH₂CH₂NH₂ + HBr
- (ii) n-Propylalcohol: Convert to propyl bromide first, then react as above.
- (iii) n-Butylalcohol: Shorten chain by oxidation to butanal, convert to propanal and then to n-propylamine.
- (iv) Propanenitrile: CH₃CH₂CN + 2H₂ ----> CH₃CH₂CH₂NH₂ (hydrogenation)
- 9 (c) In two steps, describe how to convert benzene into aniline (phenylamine):
- 1. Nitration: $C_6H_6 + HNO_3 ----> C_6H_5NO_2 + H_2O$
- 2. Reduction: $C_6H_5NO_2 + 6[H] ----> C_6H_5NH_2 + 2H_2O$
- 9 (d) Reactions of phenylamine:
- (i) With ethanoic anhydride:

$$C_6H_5NH_2 + (CH_3CO)_2O ----> C_6H_5NHCOCH_3 + CH_3COOH$$

Product: Acetanilide

(ii) With aqueous bromine:

 $C_6H_5NH_2 + 3Br_2 ----> 2,4,6$ -tribromoaniline + 3HBr

(iii) Ethanoic anhydride followed by bromine water:

Acetanilide formation first, then bromination at para position.

(iv) With sodium nitrite and hydrochloric acid below 10°C:

$$C_6H_5NH_2 + HNO_2 + HC1 ----> C_6H_5N_2 + C1 - + 2H_2O$$

Product: Benzenediazonium chloride

10 (a) Arrange the following compounds in the order of increasing acidic strength:

10

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(i) Phenol, Benzyl alcohol, Benzoic acid, Nitrobenzoic acid Increasing acidity:

Benzyl alcohol < Phenol < Benzoic acid < Nitrobenzoic acid

Reason: Electron-withdrawing NO₂ group increases acidity of benzoic acid, while benzyl alcohol is the least acidic due to lack of resonance stabilization of its conjugate base.

(ii) Ethanoic acid, Propanoic acid, Methanoic acid, 2-chloroethanoic acid, 2-methylpropanoic acid Increasing acidity:

2-methylpropanoic acid < Propanoic acid < Ethanoic acid < Methanoic acid < 2-chloroethanoic acid Reason: Electron withdrawing groups (like Cl) increase acidity, while electron donating groups (like CH₃) decrease it.

10 (b) Provide the major products of the following reactions:

10 (c) A compound with the following structural formula:

(i) With nitrous acid (HNO₂):

Reaction with primary amine produces nitrogen gas, alcohol, water, and carboxylic acid derivative: $H_2N-CHR-COOH+HNO_2---->HO-CHR-COOH+N_2+H_2O$

(ii) With ethanol:

Forms ester via esterification: -COOH group reacts with ethanol:

$$R-COOH + C_2H_5OH ----> R-COOC_2H_5 + H_2O$$

(iii) With LiAlH₄:

Reduces both –COOH and –C=O groups to alcohols:

Product will be: CH₂OH–CHR–CH₂OH

(iv) With potassium dichromate:

Oxidizes –OH groups or α -keto acid group (if present) to dicarboxylic acid.

(v) With PCl₅:

Carboxylic group is converted to acid chloride: R-COCl, ketone remains unchanged.

10 (d) Briefly explain the uses and hazards of carboxylic acids.

Uses:

Used in food preservatives (e.g., benzoic acid), production of polymers, esters, solvents, and in pharmaceuticals.

Hazards:

Carboxylic acids are corrosive, can irritate skin and mucous membranes, and some volatile acids (e.g., formic acid) can affect respiratory system.