THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Year: 2004**

Instructions

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

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1 (a) Explain the following of a cell formed by combining $Zn^{2+}(aq)/Zn(s)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells. Indicate on the sketch the following:

(i) The positive electrode

The Cu^{2+}/Cu is the positive electrode (cathode).

(ii) The direction of electron flow in the external circuit

Electrons flow from Zn (anode) to Cu (cathode).

(iii) The electrode at which oxidation occurs

Oxidation occurs at Zn electrode (anode).

(b) Calculate the e.m.f of the cell operating under standard conditions:

E°cell = E°cathode - E°anode

= $E°Cu^{2+}/Cu$ - $E°Zn^{2+}/Zn$

= 0.34 V - (-0.76 V) = 1.10 V

(c) Explain how the e.m.f of the cell would be affected by:

(i) Increase in $[Cu^{2+}]$

E.m.f increases since the cathode reaction is favored.

(ii) Increase in $[Zn^{2+}]$

E.m.f decreases since the anode reaction is favored (Le Chatelier's principle).

(d) If the $Zn^{2+}(aq)/Zn(s)$ electrode system was replaced by $Ag^{+}(aq)/Ag(s)$, what would the e.m.f of the cell be?

E°cell = $E°Ag^{+}/Ag$ - $E°Cu^{2+}/Cu$

= 0.80 V - 0.34 V = 0.46 V

2 (a) Explain the meaning of the following terms:

(i) Zero order reaction: A reaction whose rate is independent of the concentration of the reactants.

(ii) Rate law: An equation that relates the rate of reaction to the concentration of reactants.

(iii) Energy profile: A diagram showing energy changes during a reaction pathway, highlighting activation energy and transition states.

(b) For a reaction A + 2B ---> Products, with the following data:

Experiment	[A] mol dm^{-3}	[B] mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
1	4.0×10^{-3}	4.0×10^{-3}	6.5×10^{-5}
2	4.0×10^{-3}	8.0×10^{-3}	1.28×10^{-4}
3	8.0×10^{-3}	4.0×10^{-3}	2.6×10^{-4}
4	8.0×10^{-3}	8.0×10^{-3}	5.12×10^{-4}

Order with respect to B:

Compare 1 and 2: Rate doubles, [B] doubles → first order in B.

Order with respect to A:

Compare 1 and 3: Rate increases 4 times, [A] doubles → second order in A.

Overall order: 2 (A) + 1 (B) = 3

Rate constant k = Rate / $[A]^2[B]$

Using experiment 1:

$k = 6.5 \times 10^{-5} / (4.0 \times 10^{-3})^2 \times (4.0 \times 10^{-3})$

$= 6.5 \times 10^{-5} / (6.4 \times 10^{-8}) = 1015.63$ mol^{-2} dm^{6} s^{-1}

Units of k: mol^{-2} dm^{6} s^{-1}

3 (a) How does calcium hydroxide react with:

(i) Carbon dioxide: $Ca(OH)_2 + CO_2$ ---> $CaCO_3 + H_2O$

(ii) Ammonium salt: $Ca(OH)_2 + NH_4Cl$ ---> $CaCl_2 + NH_3 + H_2O$

(iii) Temporary hard water: $Ca(OH)_2 + Ca(HCO_3)_2$ ---> $2CaCO_3 + 2H_2O$

(b) Explain what happens and show reactions when:

(i) Excess chlorine gas is passed through hot concentrated NaOH:

$Cl_2 + 2NaOH$ ---> $NaCl + NaClO + H_2O$

(ii) Concentrated aqueous ammonia falls drop by drop into chlorine gas:

$2NH_3 + Cl_2$ ---> $N_2 + NH_4Cl$

(iii) Excess HCl added to $PbCl_2$ solution:

$PbCl_2 + 2Cl^-$ ---> $[PbCl_4]^{2-}$ (complex ion formed)

(iv) Solid ammonium chloride heated:

NH_4Cl ---> $NH_3 + HCl$

(c) Complete and balance the equations:

(i) $NaH + H_2O$ ---> $NaOH + H_2\uparrow$

(ii) $CaC_2 + H_2O$ ---> $C_2H_2 + Ca(OH)_2$

(iii) $H_2S + H_2SO_4$ ---> $S + SO_2 + H_2O$

4 (a)(i) Lewis acid: A substance that accepts a pair of electrons to form a covalent bond.

(ii) Conjugate base: The species formed after an acid donates a proton.

(iii) Kohlrausch's Law: The molar conductivity of an electrolyte at infinite dilution is equal to the sum of the ionic conductivities of its individual ions.

(iv) Meaning of dilution (v): It refers to the volume at which the solution is diluted in the formula $\Lambda v = \kappa v$

(b) During $KMnO_4$ titration, no indicator is needed since $KMnO_4$ is self-indicating (it changes color). In iodometry, starch is used as an indicator and added near the endpoint to avoid formation of stable starch-iodine complex prematurely.

(c) (i) In Arrhenius equation k = Ae^(-Ea/RT), k is rate constant, A is frequency factor, Ea is activation energy, R is gas constant, and T is temperature.

(ii) Table completion is already provided, plotting ln(k) against 1/T will give a straight line with slope = -Ea/R. Use slope to calculate Ea.

(iii) Slope = -Ea/R, Ea = -slope × R

(d) Molar conductivity (Λm) = κ / c

= $1.29\ S\ m^{-1} / 0.1\ mol\ m^{-3} = 12.9\ S\ m^2\ mol^{-1}$

5 (a)(i) Pentavalent phosphorus compounds are stable due to d-orbital participation, while nitrogen lacks d-orbitals, limiting to trivalent forms.

(ii) $AlCl_3 \cdot 6H_2O$ releases H^+ in solution (acidic), while CH_3COONa forms OH^- (basic).

(iii) Nitric acid is corrosive, but Al forms oxide coating which protects it.

(iv) $CaCO_3$ is insoluble, but reacts with $CO_2 + H_2O$ forming soluble $Ca(HCO_3)_2$.

(b) $KMnO_4$ oxidizes oxalic acid to CO_2

(i) Half reduction: $MnO_4^- + 8H^+ + 5e^-$ ---> $Mn^{2+} + 4H_2O$

(ii) Half oxidation: $H_2C_2O_4$ ---> $2CO_2 + 2H^+ + 2e^-$

(iii) Net equation: $2MnO_4^- + 5H_2C_2O_4 + 6H^+$ ---> $2Mn^{2+} + 10CO_2 + 8H_2O$

(c) Calculate mass of iodine

$KIO_3 + 5KI + 6HCl$ ---> $3I_2 + 3H_2O + 6KCl$

Molar mass KIO_3 = 214 g/mol

Moles = 107 g / 214 = 0.5 mol

From equation: 1 mol KIO_3 gives 1.5 mol I_2

0.5 mol KIO_3 gives 0.75 mol I_2

Mass of I_2 = 0.75 mol × 254 g/mol = 190.5 g

6 (a)(i) Write down the stable electronic configuration of Cr, Cu^{2+} and N

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Cu^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

N: $1s^2\ 2s^2\ 2p^3$

(ii) Define the term disproportionation

Disproportionation is a redox reaction in which a single species undergoes simultaneous oxidation and reduction.

(b) Which of the following reactions display disproportionation phenomenon? Give reasons:

(i) $Cl_2(g) + 2Br^-(aq)$ ---> $2Cl^-(aq) + Br_2(l)$

No, this is a displacement reaction, not disproportionation.

(ii) $2H_2O_2(aq)$ ---> $2H_2O(l) + O_2(g)$

Yes, oxygen in H_2O_2 is both oxidized (from -1 to 0) and reduced (from -1 to -2).

(iii) $CaCO_3(s)$ ---> $CaO(s) + CO_2(g)$

No, this is thermal decomposition, not a redox or disproportionation.

(iv) $2NO_2(g) + H_2O(l)$ ---> $HNO_3(aq) + HNO_2(aq)$

Yes, nitrogen in NO_2 is both oxidized (to HNO_3, +5) and reduced (to HNO_2, +3).

(c) Explain the following:

(i) The first ionization energy of oxygen is lower than that of nitrogen although oxygen is right of nitrogen.

This is due to electron-electron repulsion in the paired 2p orbitals of oxygen, making it easier to remove an electron.

(ii) The chemistry of magnesium resembles that of lithium although they are in different groups.

This is due to diagonal relationship; both are small, have similar polarizing power and form similar compounds.

(iii) Silicon has a much higher melting point than expected.

Due to strong covalent bonding in its giant tetrahedral structure, high energy is needed to break the bonds.

(iv) Graphite is used as a lubricant as well as in electrodes but not diamond.

Graphite has delocalized electrons for conduction and layers that slide easily. Diamond is a hard insulator with no free electrons.

7 (a)(i) Define nuclear fission with an example and applications.

Nuclear fission is the splitting of a heavy nucleus (e.g., U-235) into smaller nuclei with release of energy.

Example: ^{235}U + n ---> Ba + Kr + 3n + energy

Applications: electricity generation, nuclear weapons, medical isotopes.

(ii) Chlorine consists of two isotopes: ^{35}Cl (75.77%) and ^{37}Cl

Relative atomic mass = (75.77×35 + x×37)/100 = 35.453

Solve for x:

35.453 = (75.77×35 + x×37)/100

3545.3 = 2651.95 + 37x

37x = 893.35

x = 24.13% ----> relative abundance of ^{37}Cl = 24.13%

(b) Explain briefly the meaning of the following quantum numbers:

(i) n – principal quantum number (energy level)

(ii) l – azimuthal quantum number (subshell shape)

(iii) m – magnetic quantum number (orbital orientation)

(iv) ms – spin quantum number (electron spin)

(c) (i) Given n = 2, possible orbitals are 2s and 2p

(ii) l can be 0 or 1; m values for l=1 are -1, 0, +1; ms = +½ or -½

8 (a)(i) Differentiate amines from amides:

Amines have $–NH_2$ or $–NR_2$ group attached to carbon; amides have $–CONH_2$ group.

(ii) Reaction of amines with mineral acids is similar to ammonia:

RNH_2 + HCl ---> $RNH_3^+Cl^-$ (same as NH_3 + HCl ---> $NH_4^+Cl^-$)

(b) Preparation reactions:

(i) Benzene ----> Phenylamine:

Benzene ----> Nitrobenzene (HNO_3/H_2SO_4)

Nitrobenzene ---> Phenylamine (Sn/HCl or Fe/HCl, then NaOH)

(ii) Benzene ----> 3-Nitromethylbenzene:

Step 1: Benzene ---> Toluene ($CH_3Cl/AlCl_3$)

Step 2: Toluene ---> 3-nitrotoluene (HNO_3/H_2SO_4)

(c) Rewriting incorrect conditions:

(i) $CH_3CH_2CHO + H_2$ ---> $CH_3CH_2CH_2OH$ (correct: H_2/Ni or H_2/Pt)

(ii) $CH_3OH + CH_3COOH$ ---> $CH_3COOCH_3 + H_2O$ (correct: H^+ catalyst)

(iii) $CH_3CH_2OH + NaHCO_3$ ---> no reaction (correct acid is needed, not alcohol)

(iv) Benzene + $Cl_2/AlCl_3$ ----> Chlorobenzene

(v) Phenol + CH_3COOH ---> Ester (correct: H^+ catalyst)

(d) (i) Separation process:

- Flask A: 4-methylphenylamine (forms water soluble salt with HCl)

- Flask B: 4-methylbenzenecarboxylic acid (reacts with $NaHCO_3$)

- Flask C: N-phenyletharamide (remains in ether)

(ii) Organic compound with Mr = 88

Possible isomers:

Aliphatic carboxylic acid: $CH_3CH_2CH_2COOH$ (Butanoic acid)

Aliphatic ester: $CH_3CH_2COOCH_3$ (Methyl propanoate)

9 (a) Benzene is said to have delocalized electrons. What does this mean?

Benzene has a ring structure with six carbon atoms where the six π electrons are not localized between individual carbon atoms but are instead shared equally over all six carbons. This delocalization forms a conjugated system resulting in a stable structure and is responsible for benzene’s unique reactivity and stability.

9 (b) Compare and contrast the reactions of benzene, cyclohexene, and cyclohexane using bromine gas as a reagent.

- Benzene undergoes electrophilic substitution with bromine in the presence of a catalyst ($FeBr_3$ or $AlBr_3$) due to its delocalized π electrons.

C_6H_6 + Br_2 ----> C_6H_5Br + HBr

- Cyclohexene undergoes electrophilic addition readily with bromine without a catalyst. The reddish-brown color of bromine disappears.

C_6H_{10} + Br_2 ----> $C_6H_{10}Br_2$

- Cyclohexane does not react easily with bromine under normal conditions; reaction requires UV light and results in substitution.

C_6H_{12} + Br_2 ----> $C_6H_{11}Br$ + HBr (under UV light)

9 (c) Compound P of molecular formula $C_6H_{12}O$ reacts with sodium metal to form compound T ($C_6H_{11}ONa$) with evolution of hydrogen gas. Compound P also reacts to form the following sequence:

P --(hot Al_2O_3)--> Q (C_6H_{10})

Q --(H_2/Ni, heat)--> R (C_6H_{12})

R + Cl_2 --->U ($C_6H_{12}Cl_2$)

P + HBr ---> S ($C_6H_{11}Br$)

(i) If the structural formula of U is Cl–CH_2–CH(Cl)–CH(CH_3)–CH_2–CH_3 and R cannot undergo further addition reactions, deduce the structures:

P: CH_3–CH_2–CH(OH)–CH(CH_3)–CH_2–CH_3

Q: CH_3–CH=CH–CH(CH_3)–CH_2–CH_3 (alkene by dehydration)

R: CH_3–CH_2–CH_2–CH(CH_3)–CH_2–CH_3 (alkane by hydrogenation)

T: Sodium alkoxide of P (RO^-Na^+)

(ii) Reagent A is HBr.

S = $CH_3–CH_2–CH(Br)–CH(CH_3)–CH_2–CH_3$

9 (d) Give the IUPAC names of the following organic compounds:

(i) $CH_3–CH_2–CH(CH_3)–COOH$ -----> 2-methylbutanoic acid

(ii) Benzamide ----> Benzenecarboxamide

(iii) $CH_3–CH_2–CH_2CH_2–COOCH_2CH_3$ -----> Pentanoic acid ethyl ester (Ethyl pentanoate)

(iv) $CH_3CH_2CH_2CH_2–C(CH_3)(NH_2)$ ---> 3-methylpentan-2-amine

(v) $C_6H_5–CH_2CH_2CH_2–COOH$ ----> 4-phenylbutanoic acid

10 (a) Chemical conversions:

(i) Benzene to benzoic acid

C_6H_6 ----> $C_6H_5–CH_3$ (methylation) ----> $C_6H_5–COOH$ (oxidation with $KMnO_4$)

(ii) Propanoic acid to ethanoic acid

CH_3CH_2COOH ----> CH_3CH_3 (decarboxylation using soda lime) -----> CH_3COOH (oxidation using $KMnO_4$)

10 (b) The structure of one isomer with molecular formula $C_6H_4O_2BrNO_2$ is:

2-Bromo-4-nitrophenol

Other isomers include:

1. 2-Bromo-6-nitrophenol

2. 3-Bromo-4-nitrophenol

3. 3-Bromo-2-nitrophenol

4. 4-Bromo-2-nitrophenol

5. 4-Bromo-3-nitrophenol

6. 2-Bromo-3-nitrophenol

10 (c) Arrange the following compounds in order of increasing basic strength.

(i) p-Methylaniline (C_6H_4–NH_2–CH_3)

(ii) Benzylamine (C_6H_5–CH_2NH_2)

(iii) N-methylaniline (C_6H_5–$NHCH_3$)

(iv) Aniline (C_6H_5–NH_2)

Order of increasing basic strength:

(i) < (iv) < (iii) < (ii)

Reason: Electron-donating alkyl groups increase electron density on nitrogen, enhancing basicity. However, resonance in aromatic amines reduces availability of lone pair on nitrogen, decreasing basicity. Benzylamine has no resonance withdrawal and is most basic.