2015 DHS Year 6 H2 Chemistry Preliminary Examination (Answer Scheme)

1 Planning (P)

- 1 (a) (i)
 - 1. Connect the nozzle of hydrogen gas can to the effusion hole of a 100 cm³ wellgreased syringe using rubber tubing.
 - 2. Flush the syringe with hydrogen at least once before filling the syringe with hydrogen gas at constant temperature of 25 °C. Piston should be above the start volume.
 - 3. Detach the tubing from the effusion hole and allow hydrogen gas to effuse out. (Free movement, not pushed to start mark.)
 - 4. Start the stopwatch when the piston passes the 80 cm³ mark on the syringe and stop the stopwatch when the piston falls to 30 cm³ mark on the syringe. Start the stopwatch when the piston passes the 80 cm³ mark on the syringe and stop the stopwatch after 10 minutes.
 - 5. Repeat step 1 4 with another sample of hydrogen gas and obtain the average effusion time \overline{OR} volume at constant temperature of 25 °C.
 - 6. Repeat step 1 4 with the four other gases (butane, oxygen, carbon dioxide and chlorine gas) at constant temperature of 25 °C.

| Gas | <i>M</i> r | Effusion time for expt 1 / s | Effusion time for expt 2 / s | (Average) effusion time / s | Rate of effusion / cm ³ s ⁻¹ |
|-------------------|------------|------------------------------------|------------------------------------|-----------------------------------|--|
| Hydrogen | 2.0 | | | | |
| Butane | 58.0 | | | | |
| Oxygen | 32.0 | | | | |
| Carbon dioxide | 44.0 | | | | |
| Chlorine | 71.0 | | | | |

OR

| Gas | <i>M</i> r | Effusion volume in 10 min for expt 1/ cm ³ | Effusion volume in 10 min for expt 2 / cm ³ | Average effusion volume in 10 min/ cm ³ | Rate of effusion / cm ³ min ⁻¹ |
|-------------------|------------|--|---|---|--|
| Hydrogen | 2.0 | | | | |
| Butane | 58.0 | | | | |
| Oxygen | 32.0 | | | | |
| Carbon dioxide | 44.0 | | | | |



Using the results, plot a graph of rate of effusion against M_r of the gas, read off the rate of effusion of nitrogen gas, x, at its M_r of 28.0.

(b) (i)

(ii)

Moles of $Cu(NH_3)_4SO_4$ to be formed \approx Moles of $CuSO_4$ required = 0.02196 mol

Moles of NH_3 required $\approx 4 \times Moles$ of $CuSO_4$ required = 0.08787 mol

:. Volume of CuSO₄ required = $0.02196 / 0.50 = 43.9 \text{ cm}^3$

 \therefore Volume of NH₃ required = 0.08787/ 2.0 = 43.9 cm³

(ii) Procedure

- 1. Using a 50 cm³ measuring cylinder, transfer 50 cm³ of CuSO₄ (aq) into a 150 cm³ beaker.
- 2. Using another 50 cm³ measuring cylinder, gradually add 50 cm³ of NH_3 (aq) into the 50.00 cm³ of CuSO₄ (aq), with stirring until all the solids have dissolved.
- 3. Leave the mixture to stand for 15 minutes undisturbed, so that an equilibrium can be established.
- 4. Place the beaker in an ice bath and slowly add (drop wise), using a dropper, about 30 cm³ of acetone to the beaker with continuous stirring.
- 5. Leave the solution to remain in the ice bath for about 15 minutes.
- 6. Filter off the crude product, using (vacuum) filtration (or Buchner apparatus), and wash it with a little cold acetone.
- 7. Dissolve the crude product in *minimum* volume of hot acetone in a small conical flask. When all crude product has dissolved completely, allow the solution to cool.
- 8. When recrystallisation is completed, filter off the pure product using (vacuum) filtration. Dry the crystals between filter papers then transfer them to a sample tube and leave them to dry in air.

2 (a) (i) M_r of UDMH = 60; M_r of N₂O₄ = 92

Mole ratio of UDMH : N_2O_4 is 1:2 Since total mass =244 kg = 1(60) + 2(92) Mass of UDMH used = 60 kg Moles of UDMH used = 60 000/60 = 1000 mol x = 1000

Moles of gaseous products formed = 9 x 1000 = 9000 mol

*p*V = nRT, V = nRT/*p* = 9000 (8.31) (263)/600 = 3.28 x 10⁴ m³

(ii) It is the energy change when 1 mole of (liquid) (CH₃)₂N₂H₂ is formed from its constituent elements, carbon, nitrogen and hydrogen, under standard conditions, i.e.. 298 K and 1 atm pressure.

(iii)
$$\Delta G_r = \Delta H_r - T\Delta S_r$$

 $\Delta H = \Delta G + T\Delta S$
 $= (-2107) + 298(844/1000)$
 $= -1855 \text{ kJ mol}^{-1}$
 $\Delta H_r = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$
 $-1855 = 2(-394) + 4(-242) - [x + 2(9.0)]$
 $x = +81.0 \text{ kJ mol}^{-1}$

(b) (i) Gradient of graph = -14194 (units: K)

$$-\frac{E_a}{R} = -14194$$

 $E_a = -14194 \times 8.31$
= 117 952 J mol⁻¹ = 118 kJ mol⁻¹

(ii) Rate =
$$k [NO_2]^2$$

 $[NO_2] = 6.0/3.0 = 2.0 \text{ mol dm}^{-3}$

Rate = $(3.16)(2.0)^2$ = 12.6 mol dm⁻³ s⁻¹

(c) (i)
$$N_2H_4(l) + 2H_2O_2(l) \longrightarrow 4H_2O(l) + N_2(g)$$

 N_2H_4 is oxidised. Oxidation state of N changes from -2 in N_2H_4 to O in N_2 .

(ii) Anode : $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode : $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

(iii) $E_{\text{cell}}^{\ominus} = E_{\text{red}}^{\ominus} - E_{\text{oxid}}^{\ominus}$

 $+1.75 V = 1.77 - E_{\text{oxid}}^{\ominus}$ $E_{\text{oxid}}^{\ominus} = +0.02 V$

i.e. $E^{\ominus}(CO_2/CH_3OH)$ is +0.02 V. If written as $E^{\ominus}(CH_3OH/CO_2) = + 0.02$ V, no credit is given.

- **3** (a) $Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + H_2(g)$
 - **(b) (i)** $K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$

$$z = \sqrt{K_{sp}}$$

- (ii) The oxalate anion is a conjugate base of the weak acid hydrogen oxalate. Since the extent of dissociation of hydrogen oxalate depends on the pH of the solution, the concentration of oxalate ion resulting from the dissociation of hydrogen oxalate will also depend on the pH of the solution. Therefore, the term K_2 must be taken into account when considering the solubility of oxalate. The term $[H^+]$ is to account for the pH of the solution that calcium oxalate is subjected to.
- (iii) The solubility of calcium oxalate will increase with decreasing pH value (can be inferred from the given equation due to the increase in [H⁺].) At low pH, oxalate ions will be protonated to form hydrogen oxalate ions. This will reduce the concentration of oxalate ions. By Le Chatelier's principle, the solubility product equilibrium of calcium oxalate will shift to increase the concentration of oxalate ions. Hence, the solubility of calcium oxalate will increase.
- (iv) Sodium hydroxide might precipitate calcium hydroxide which would decrease the concentration of calcium ions thereby potentially increasing the solubility of calcium oxalate at high pH.

(c) (i)
$$CH_3CH(NH_2)COOH + 3O_2 \longrightarrow \frac{5}{2}CO_2 + \frac{5}{2}H_2O + \frac{1}{2}CO(NH_2)_2$$

 $\overrightarrow{OR} CH_3CH(NH_2)COOH + 6[O] \longrightarrow \frac{5}{2}CO_2 + \frac{5}{2}H_2O + \frac{1}{2}CO(NH_2)_2$

(ii) Moles of alanine in 1.00 g =
$$\frac{1}{89}$$
 = 0.01123 mol



By Hess' Law,

 $\Delta H_{\rm rxn} = -1577 + 632 = -945 \text{ KJ mol}^{-1}$

Hence, amount of energy evolved = 945 × 0.01123 = 10.6 kJ





- (b) Volume of hydrogen gas
 - Ammeter reading / Current
 - Time taken
- (c) Amount of hydrogen gas = 0.210 / 24 = 0.00875 mol Q = It = (5.6)(5 x 60) = 1680 C Quantity of charge per mole of hydrogen gas = 1680 / 0.00875 = 1.92×10^5 C
- (d) Q = 2Le $1.92 \times 10^5 = (2)(L)(1.60 \times 10^{-19})$ L = 6.00 x 10^{23}

- (e) There is resistance in the circuit / Heat loss due to resistance.
- **5 (a) (i)** On going across Period 3, the hydroxides go from basic to acidic. This systematic variation is the result of (1) increasing electronegativity of the elements, which leads to (2) the difference in the bonding between the elements and the hydroxide.
 - Going across Period 3, an increase in the effective nuclear charge of the elements, resulting in the increase in their electronegativity.
 - *Difference in electronegativity* between the elements and the hydroxide becomes smaller on going across the Period 3 hydroxides, resulting in the bonding between them changing from ionic to covalent.
 - Ionic oxides/hydroxides are basic because of the presence of OH⁻ ions, and the covalent oxides/hydroxides are acidic due to the interactions of the partially positive elements with water, releasing H⁺ ion.

(ii)

| Cl(OH) or HOCl or HClO | |
|---------------------------|--|
| | |

(b) Only 1–chlorobut–2–ene undergoes nucleophilic substitution/ hydrolysis with NaOH(aq) and form AgC*l* white ppt.

The C–C*l* bond in 2–chlorobut–2–ene is harder to break due to overlap of chlorine's p orbital with the unhybridised p orbitals of the carbon atoms in the C=C bond which strengthens the bond. Hence, no free C*l* ions are formed to react with Ag⁺ to form AgC*l* white ppt.

- (c) (i) $Cu^+(g) \longrightarrow Cu^{2+}(g) + e^-$
 - (ii) The second electron removed from zinc is a 4s-electron / 4th principal quantum shell while the second electron removed from copper is a 3d-electron / 3rd principal quantum shell. Since a 3d-electron from the 3rd principal quantum shell has lower energy, more strongly attracted to the nucleus, hence, a greater energy is required to remove it, causing second ionisation energy of Cu to be higher than that of Zn respectively.
- 6 (a) (i) Nucleophile is OH^- / hydroxide ion.



(ii) acid-base

- (b) (i) All three substances are covalent compounds with simple molecular structures.
 - A larger amount of energy is needed overcome strong hydrogen bonds between CH₃OH molecules than the weaker van der Waals' interactions between CH₃SH or CH₃SeH molecules.
 - Thus CH₃OH has the highest boiling point.
 - Number of electrons in CH₃SeH is larger than that in CH₃SH.
 - CH₃SeH is more easily polarised to form larger dipoles than CH₃SH.
 - A larger amount of energy is needed to overcome stronger van der Waals' interactions
 - Thus CH₃SeH has a higher boiling point than CH₃SH.
 - (ii) Strongest CH₃SeH > CH₃SH > CH₃OH Weakest

(Z = O, S or Se)

- Size of atom decreases from Se to O.
- Z–H bond length decreases from Se–H to O–H.
- Bond strength increases from Se–H to O–H.
- Ease of breaking Z–H bond decreases from Se to O.

(c)



- 7 (a) From data, reaction mixture loses optical activity completely when 50 % of the reactants have been incorporated with ^{131}I . \Rightarrow 50 % of reactants have become non-superimposable mirror images of the other 50 % of unreacted molecules, so that the resulting mixture is optically inactive.
 - This means that the nucleophile attacks the electrophilic C atom from the opposite side

of the I atom,

- so that each reacting 2-iodooctane undergoes an inversion of stereochemical configuration to become its optical isomer.
- Thus reaction follows an $S_N 2$ mechanism.

