1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
С	В	С	D	Α	С	Α	С	Α	D	С	С	Α	С	Α	D	Α	В	D	В
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40

Paper 1 MCQ Answers:

Paper 2

1(a)

 $Mg^+(g) \rightarrow Mg^{2+}(g) + e^{-1}$ (i)

The second ionisation involves removal of an electron from the 3p subshell from Si⁺, and the (ii) 3s subshell from Al⁺. Since the 3p subshell is on average further from the nucleus / at a higher energy level / experiences more shielding than the 3s subshell, the electron removed from Si⁺ is less tightly held and requires less energy to remove.

Neon, being already in the gaseous state, is ionised first and emits light, (b) whereas sodium is in the solid state and takes time to vaporise before it can be ionised. OR Neon has a higher first ionisation energy than sodium. The initial power surge when the light is turned on is able to ionize neon, giving rise to the red light, after which the power drops and is only enough to ionise sodium, giving rise to the orange light.

(C)

- (i) Al₂O₃ has a giant ionic lattice structure with strong ionic bonds / high lattice energy / partial covalent character, hence it is insoluble. SiO₂ has a giant molecular structure with strong covalent bonds requiring large amounts of energy to break, hence it is insoluble.
- A/Cl_3 dissolves to give $[A/(H_2O)_6]^{3+}$ (aq) which undergoes hydrolysis due to the high charge (ii) density on Al^{3+} : $[Al(H_2O)_6]^{3+} \rightarrow [Al(H_2O)_5(OH)]^{2+} + H^+$ $OR 2AlCl_3 + 6H_2O \Rightarrow Al_2O_3 + 6HCl$ $OR AlCl_3 + 3H_2O \Rightarrow Al(OH)_3 + 3HCl$ SiC l_4 hydrolyses in water to give HC l_1 , a strong acid / H⁺ is produced: $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ <u>OR</u> SiC l_4 + 4H₂O \rightarrow Si(OH)₄ + 4HCl

(d)

Solubility of Li₂O is lower than that of BaO. (i) Therefore, the basicity of Li₂O is also lower than that of BaO.

(ii) Percentage change in mass
=
$$\frac{[2(6.9) + 12.0 + 3(16.0)] - [2(6.9) + 2(16.0)]}{[2(6.9) + 2(16.0)]} \times 100\%$$

= 61.1%

2(a)

 $NH_4NO_3(I) + aq \rightarrow NH_4NO_3(aq)$ 71 50 $NH_3(g) + HNO_3(g)$ -31 + 37 \checkmark NH₃(aq) + HNO₃(aq) [Total: 12]

From energy cycle, show x = 71 -31 + 37 -50 = $+27 \text{ kJ mol}^{-1}$

- (b) The reaction is <u>endothermic</u> as the temperature of the reaction mixture drops. ΔS is positive as the number of gaseous molecules increase from 0 to 1. Since reaction is spontaneous, $\Delta G < 0$. $\Delta G = \Delta H - T\Delta S$, $-T\Delta S$ must be <u>more negative</u> than ΔH .
- (C)
- (i) Undergoes substitution
- (ii)



3(a) Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ or [Ar] $3d^5 4s^1$ Cr³⁺: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ or [Ar] $3d^3$

- (b)
- (i) Cr S N Mols 0.298 1.19 2.09 Ratio 1 4 7 x + y + 1 = 7 x: 4 y:
- (ii) **+3**
- (iii)



2

(i) $K_2Cr_2O_7 + 2 HBr \rightarrow 2 KCrO_3Br + H_2O$

- (ii) No, oxidation no. of Cr doesn't change, remains at +6
- (iii) $E_{cell}^{e} = +1.33 (+1.07) = +0.26 \text{ V} >0$ Products should be **Cr³⁺(aq) and Br₂(l)**
- (iv) Reaction didn't take place at standard condition. OR The reaction in step I took place under cooled conditions.

(v) AgBr

(vi) Cr is **reduced** from +6 (orange solution of $Cr_2O_7^{2-}$) to +3 Cr³⁺ (deep green solution)

[Total: 16]

4 (a)

 $p_{H_2} = (\frac{0.055}{0.1}) \times 1.5 \text{ atm} = 0.825 \text{ atm}$ $p_{H_2O} = (\frac{0.045}{0.1}) \times 1.5 \text{ atm} = 0.675 \text{ atm}$

$$K_{p} = \frac{(p_{H_2})^4}{(p_{H_2O})^4} = \frac{(0.825)^4}{(0.675)^4}$$
$$= 2.23$$

(b) Formation of ammonia is **<u>exothermic</u>**.

... <u>Low temperature</u> is used to obtain higher yield of ammonia. Since, low temperature is used, the rate of formation of ammonia is <u>slow</u>. Hence, catalyst is used to increase rate.

Formation of nitrogen dioxide is <u>endothermic</u>.
 ∴ <u>High temperature</u> is used to obtain higher yield of nitrogen dioxide.
 Since, high temperature is used, the rate of formation of nitrogen dioxide is <u>fast</u>. Hence, catalyst is not required.

(C)

(i) Step I: conc HNO₃ and conc H_2SO_4 , 30 °C

Step II: excess Cl₂, uv light

(ii) Step IV: Elimination (of water) / Dehydration Step VII: Electrophilic substitution







- (iii) Add KMnO₄/H⁺ (aq) and heat to both samples. For chloroxylenol, purple KMnO₄ is decolourised, but not for 4-chlorophenol.
- (b)
- (i)

reagents & conditions	type of reaction	organic products
concentrated D ₂ SO ₄ , heat	Dehydration / elimination (of water)	H-C=CH ₂ CI



(ii) No (orange) ppt is observed.Z is not a carbonyl compound (is not an aldehyde or ketone)

[Total: 10]

Paper 3

1(a)

- (i) $KNO_3 \rightarrow KNO_2 + \frac{1}{2}O_2$
- (ii) $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2}O_2$ \underline{NO}_2 , which is produced from decomposition of magnesium nitrate, is <u>toxic/a pollutant</u>. <u>OR</u> Decomposition of magnesium nitrate occurs <u>more readily</u> than potassium nitrate, resulting in a loss in <u>control of burning rate</u> at the high temperatures reached in fireworks. OR

Potassium nitrate releases more mols of O_2 per mass than magnesium nitrate because of its lower M_r .

(b) Let the unknown Group II metal be **M**.

 $2 \text{ Al} + \frac{3}{2}\text{ O}_2 \rightarrow \text{Al}_2\text{ O}_3$ No. of mols of $\text{O}_2 = \frac{0.0141}{2} \times \frac{3}{2} = 0.01058$ Mass of KNO₃ = 2 × 0.01058 [39.1 + 14.0 + 3(16.0)] = 2.138 g Mass of MCO₃ = 2.75 - 2.138 = 0.612 g MCO₃ \rightarrow MO + CO₂ No. of mols of CO₂ = $\frac{100}{24000} = 4.167 \times 10^{-3}$ M_r(MCO₃) = $\frac{0.612}{4.167 \times 10^{-3}} = 146.9$ A_r(M) = 146.9 - 12.0 - 3(16.0) = 86.9 \approx 87.6 Therefore, M is strontium.

(c) (i)

 P^{3-} has a larger radius than S^{2-} . P^{3-} has a <u>smaller nuclear charge but the same number of electrons</u> as S^{2-} , hence the electrons experience less attraction to the nucleus and spread out over a larger volume.

- (ii) State: PCl₅ or phosphorus in oxidation state <u>+5</u> Phosphorus is able to <u>expand its octet</u> to accommodate 5 electron pairs as it is in <u>Period 3</u> and thus has empty 3d orbitals of similar energy, whereas nitrogen, being in Period 2, does not have suitable orbitals of similar energy for this purpose.
- (d) Test: To each of the compounds, add Br₂(aq). Observation: Both gallic and shikimic acids will decolorize bromine. However, only <u>gallic</u> acid will give a white precipitate, while <u>shikimic acid will not</u>. <u>OR</u> Test: To each of the compounds, add neutral FeCl₃(aq). Observation: Only gallic acid will give a <u>violet colouration</u>, whereas shikimic acid will give

no visible observation.



 (ii) (Chloromethyl)benzene is <u>hydrolysed/</u>undergoes <u>nucleophilic substitution</u> to give <u>free CF</u>, <u>which is precipitated as AgCI</u> on addition of aqueous AgNO₃(aq). <u>OR</u>

<u>balanced</u> equations for nucleophilic substitution and precipitation reactions 2-chloromethylbenzene does not react due to the <u>partial double bond character</u> of the C-C*l* bond, which results from the <u>delocalization of the C*l* lone pair into the ring</u>. (Fluoromethyl)benzene does not react due to the <u>strong C-F bond</u>, which is resistant/inert to nucleophilic substitution.

[Total: 20]

2(a) (i)

n-butane has a

OR n-butane is a straight chain while i-butane is branched. Stronger / more extensive intermolecular van der Waals' forces exist in n-butane.

= mc∆T

(ii) methylpropane / 2-methylpropane

- (iii) i-butane is inert / unreactive / stable.
 OR C-H bonds are strong
 OR butane is destroyed before reaching the stratosphere
- (iv) Amt of heat absorbed by water

Amt of heat released by burner

Mass of n-butane used

Amt of butane used

 $= \frac{100}{85} \times 315 = 371 \text{ kJ}$ $= \frac{371}{2877} = 0.129 \text{ moles}$ $= 0.129 \times 58.0 = 7.47 \text{ g}$

= (1000)(4.2)(75) = 315 kJ

(v)

 $CH_3CH_2CH_2CH_2Cl$



Mechanism: Free radical substitution

(b)

(i) Pass chlorine gas into hot aq. sodium hydroxide OR Heat NaClO. $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$ CJC: H2 CHEMISTRY 2009 Preliminary Exam ANSWERS $3ClO^2 \rightarrow 2Cl^2 + ClO_3^2$

- (ii) $ClO_3^{-} + H_2O \rightarrow ClO_4^{-} + 2H^+ 2e^-$ Overall: $4ClO_3^{-} \rightarrow 3ClO_4^{-} + Cl^-$
- (iii) pH independent. H^+ or OH⁻ is not involved in the overall equation.

[Total: 20]

3(a) $S_2O_3^{2^2}$ reacts with the I_2 produced and suppresses visible change. $2 S_2O_3^{2^2} + I_2 \rightarrow S_4O_6^{2^2} + 2 I^2$ When I_2 produced **exceeds amount of S_2O_3^{2^2} added**, starch turns the solution **blue-black** due to presence of I_2 formed and the time can be recorded.

(b) (i)

Using Expts 1 and 2, When the $[H_2O_2]$ is doubled, the initial rates of the expts also doubled, $\frac{\text{Initial rate of expt 2}}{\text{Initial rate of expt 1}} = \frac{2.5 \times 10^{-4}}{1.2 \times 10^{-4}} = 2.08 \approx 2.$ Thus, the order of reaction wrt $[H_2O_2]$ is 1.

Using Expts 2 and 3,

When the [I⁻] is doubled, the initial rates of the expts also doubled, $\frac{\text{Initial rate of expt 3}}{\text{Initial rate of expt 2}} = \frac{4.7 \times 10^{-4}}{2.5 \times 10^{-4}} = 1.88 \approx 2.$ Thus, the order of reaction wrt [I⁻] is 1.

Using **Expts 3 and 4**, where $[H_2O_2]$ and $[I^-]$ are constant at 0.20 mol dm⁻³, with the different pH 5 and 4 respectively, the initial rates of the expts are $\approx 0.47 \times 10^{-3}$ and thus, are more or less constant. Thus, order of reaction wrt [H⁺] is zero at pH 4-5. Rate = k[H_2O_2][I⁻] at pH 4-5.

- (ii) Using Expt 1, k = $\frac{1.2 \times 10^{-4}}{(0.1)(0.1)} = 0.012$ k ≈ 0.012 dm³ mol⁻¹ s⁻¹
- (iii) Using Expts 5 and 6, $pH = 0.53 \implies [H^+]_{expt 5} = 0.295 \text{ mol } dm^{-3}$ $pH = 0.40 \implies [H^+]_{expt 6} = 0.398 \text{ mol } dm^{-3}$ $\frac{[H^+]_{expt6}}{[H^+]_{expt5}} = \frac{0.398}{0.295} = 1.35$ $\frac{\text{Initial rate of expt } 6}{\text{Initial rate of expt } 5} = \frac{2.8 \times 10^{-3}}{2.1 \times 10^{-3}} = 1.33$

When the $[H^{\dagger}]$ increases by 1.35, the initial rates of the expts also increases by 1.33, Thus, the **order of reaction wrt [H^{\dagger}] is 1** at low pH.

Rate = $k'[H_2O_2][I][H^+]$ at low pH.

(iv) The mechanism of the same reaction at different pH conditions are different.

At pH=3-5, rate is independent on the $[H^+]$ but when pH gets too low, rate becomes dependent on $[H^+]$.

- (C)
- (i) Since K_{stab} of [Fe(CN)₆]³⁻ is larger than [Fe(SCN)(H₂O)₅]²⁺, [Fe(CN)₆]³⁻ is the more stable complex. Ligand exchange will occur. **Deep red solution turns orange yellow**.
- (d) No. of mols of Ag added = $0.50 / 108 = 4.63 \times 10^{-3}$

Quantity of charge = $(4.63 \times 10^{-3}) \times 96500 = 447$ C

Time taken = 447 / 0.2 = 2230 s = 37.2 min

[Total: 20]

4(a)

(i)
$$[H^+] = \sqrt{2.9 \times 10^{-14}} = 1.70 \times 10^{-7} \text{ mol dm}^{-3}$$

 $\therefore \text{ pH} = -\log(1.70 \times 10^{-7}) = 6.77$

- (ii) Neutral, as $[H^+] = [OH^-]$
- (iii) $H_2O(I) \iff H^+(aq) + OH^-(aq)$

As temperature increases, K_w increases; so the equilibrium position shifts to the right. Therefore, the forward reaction (dissociation of water) is **<u>endothermic</u>**.

(b)
$$CH_3CH_2NH_3^+ + H_2O \iff CH_3CH_2NH_2 + H_3O^+$$

pK_b = 3.25
- log K_b = 3.25
∴ K_b = 5.62 × 10⁻⁴ mol dm⁻³
∴ K_a =
$$\frac{K_w}{K_b} = \frac{2.9 \times 10^{-14}}{5.62 \times 10^{-14}} = 5.16 \times 10^{-11} \text{ mol dm}^{-3}$$

$$[H^+] = \sqrt{K_a \times c} = \sqrt{5.16 \times 10^{-11} \times 0.0200}$$

= 1.02 × 10⁻⁶ mol dm⁻³

 $pH = -\log(1.02 \times 10^{-6}) = 5.99$

(C)

(i) % of N in melamine =
$$(\frac{6 \times 14}{126}) \times 100\% = 66.7\%$$

(ii) % of N in urea = $(\frac{2 \times 14}{60}) \times 100 \% = 46.7 \%$ % of N in NH₄NO₃ = $(\frac{2 \times 14}{80}) \times 100 \% = 35.0 \%$ % of N in hydrazine = $(\frac{2 \times 14}{32}) \times 100 \% = 87.5 \%$

Hydrazine is the best as the % by mass of nitrogen is the highest of all the compounds.

- (iii) Melamine is an amine / it can accept a proton due to the lone pair of electrons on the nitrogen atom / $RNH_2 + H_2O \implies RNH_3^+ + OH^-$ (basic due to presence of OH⁻).
- (iv) Melamine is less basic than ethylamine.

As the lone pairs of electrons on N atoms are delocalised into the ring, \therefore making them less available to accept a proton.

Ethylamine is more basic than melamine as the ethyl group is electron donating, \therefore it enhances the electron density on the N atom so that it can accept a proton more readily.

(d) (i)



(ii)



(iii)



(e) The immediate ppt seen suggests that the structure of the compound obtained is <u>ionic</u> in nature, with the precipitation of Ag⁺Br⁻.



(f) Hydrogen bonding



[Total: 20]





- **C** and **D** contain <u>CH₃CO-</u> group / are <u>methyl ketones</u>.
- Yellow precipitate is <u>CHI₃</u>.
- To account for formation of cyclic ester:



• Product from the esterification undergoes <u>dehydration</u> / <u>elimination</u> (of water) since there is unreacted alcohol to form **F** *or*



[Total: 20]