Pioneer Junior College H2 Chemistry Preliminary Examination 2009 Paper 2 Answer Scheme

- 1(a)(i) Relative atomic mass of an element is defined as the ratio of the average mass of one atom of the element to $\frac{1}{12}$ the mass of an atom of ¹²C.
 - (ii) Let the percentage abundance of Ga-69 be x. 69x + (1-x)71 = 69.7 x = 0.65 [1]Therefore percentage abundance of Ga-69 be 65%; percentage abundance of Ga-71 be 35%.
 - (iii) A/Cl₃ simple covalent/molecular structure

 weak temporary induced dipole-induce dipole attraction between molecules.
 PCl₅ simple covalent/molecular structure
 - permanent dipole permanent dipole attractions between molecules.

 A/CI_3 exist as dimers, with stronger id-id (due to greater no. of electrons) than pd-pd of PCI_5.

Hence m.p. of A/CI_3 is higher than PCI_5 .



- (ii) $A_{2}O_{3}$ insoluble in water ; high lattice energy(pH 7) $P_{4}O_{10} + 6H_{2}O \rightarrow 4H_{3}PO_{4}$ (pH about 2-3)
- (c)(i) $MgCO_3$ will decompose first because it is thermally less stable:
 - Mg²⁺ has smaller ionic radius than Ca²⁺
 - Mg²⁺ (higher charge density than Ca²⁺) is more polarising than Ca²⁺.
 - Mg²⁺ polarises C-O bond of CO₃²⁻ more easily/to a greater extent, weakens and breaks the C-O bon at a lower temperature

Mass of anhydrous $M(OH)_2 = 1.575 - 0.720 = 0.855 g$

Mass of water lost = 0.090 g Amount of water lost from anhydrous $M(OH)_2 = 5.00 \times 10^{-3}$

No. of moles of M(OH)₂.n H₂O = 5.00×10^{-3}

No. of moles of water from $M(OH)_2 \cdot nH_2O = 0.720/18.0 = 0.040$

5.00 x 10⁻³ mol of M(OH)₂.nH₂O \equiv 0.040 mol of H₂O 1 mol of M(OH)₂. n H₂O \equiv 8 mol of H₂O n = 8

 $M_r \text{ of } M(OH)_2 = = 171$ $A_r \text{ of } M = 137$ **M is barium**

2(a) (i)	CH ₄ (g)	+ H ₂ O (g)	🔶 CO(g)	+ 3H ₂ (g)
Initial/atm	1	1	0	0
∆/atm	- 0.43	-0.43	+0.43	+(0.43) x 3
Equilibrium/atm	0.57	<u>0.57</u>	0.43	<u>1.29</u>

Total Pressure = 0.57 + 0.57 + 0.43 + 1.29 = 2.86 atm

(ii)
$$K_p = \frac{(p_{CO})(p_{H_2})^3}{(p_{CH_4})(p_{H_2O})}$$
 [1m] $K_p = \frac{2.84atm^2}{2}$

- (iii) 1. By Le Chatelier's Principle, <u>the position of equilibrium will shift to the right</u> to remove some of the added heat. The forward endothermic reaction is favoured; as a result, there will be higher $p_{products} \propto$ [products] and lower $p_{reactants} \propto$ [reactants]. Hence K_{p} increases with increasing temperature
 - 2. K_p remains constant as long as temperature is kept constant. Not affected by change in total pressure.
- (b) (i) Comparing expt A and B, when [H₂] is halved, keeping [NO] constant, rate is also halved. Order of reaction wrt H₂ is 1.

Substitute data from expt A and C into rate = $k[H_2][NO]^a$ where a = order of reaction wrt NO.

$$\frac{2.4 \times 10^{-6}}{1.62 \times 10^{-4}} = \frac{k(0.0100)(0.025)^{a}}{k(0.0750)(0.075)^{a}}$$

a = 2
Rate = k[H₂][NO]²



NO has an unpaired electron and is reactive; can dimerise readily to form N₂O₂

2. Rate = $k_2[N_2O_2][H_2] = k_2[H_2] k_1[NO]^2$ = $k [H_2][NO]^2$

Therefore the rate equation is consistent with the proposed mechanism.

3(a)(i) 2Fe³⁺(aq) + 2l⁻(aq) → 2Fe²⁺(aq) + l₂(aq); E^{θ}_{cell} = +0.76 + (-0.54) V = +0.22 V

The reaction is energetically feasible and produces $I_2(aq)$ which forms $\underline{I_3^-(aq)}$ – the brown solution.

(ii) $\operatorname{Fe}^{2+}(\operatorname{aq}) + 6\operatorname{F}^{-}(\operatorname{aq}) \rightarrow [\operatorname{Fe}\operatorname{F}_6]^{4-}$

Ligand exchange takes place. F^- ligands replace water ligands in the iron(II) complex ion.

The $[FeF_6]^{4-}(aq)$ ion then reduces the brown iodine to colourless iodide. Thus the brown colour fades.

$$\begin{split} &I_2(aq) + 2[FeF_6]^{4-}(aq) \rightarrow 2I^{-}(aq) + 2[FeF_6]^{3-}(aq); \\ &E^{\theta}_{cell} = +0.54 + (-0.40) \ V = +0.14 \ V \end{split}$$

(b) (i) $Fe(IO_3)_3(s) + aq \implies Fe^{3+}(aq) + 3IO_3^{-}(aq)$

 $[Fe^{3^+}] = 3.6/(580.8) = 6.20 \times 10^{-3} \text{ mol dm}^{-3}$ $[IO_3^-] = 3 \times 6.20 \times 10^{-3} = 0.0186 \text{ mol dm}^{-3}$

 $K_{sp} \text{ of } Fe(IO_3)_3 = [Fe^{3^+}]_{eqm} \times [IO_3^-]^3_{eqm}$ = **3.99x 10^-8 mol^4 dm^-12** at 298 K

(ii) Due to the Common Ion Effect, the solubility decreases.

Let the solubility be x mol dm⁻³ $[IO_3^-]_{total} = 0.105 + 3x \approx 0.105 \text{ mol dm}^{-3}$; since 3x is small compared to 0.105

$$\begin{split} & K_{sp} \text{ of } Ce(IO_3)_3 = [Ce^{3^+}]_{eqm} \times [IO_3^-]^3_{eqm} \\ & 3.99 \times 10^{-8} \text{ mol}^4 \text{ dm}^{-12} = x(0.105)^3 \text{ mol}^4 \text{ dm}^{-12} \\ & x = 3.44 \times 10^{-5} \quad (check: 3x = 1.03 \times 10^{-4} << 0.105) \end{split}$$

Solubility of $Fe(IO_3)_3$ in 0.100 mol dm⁻³ KIO₃ = <u>3.44 x 10⁻⁵ mol dm⁻³</u>.



- (b) **Step 1:** 1. Sn, concentrated HC*I*, heat under reflux 2. NaOH(aq)
 - **Step 2:** NaOH(aq), heat
 - Step 3: H₂O(g), H₃PO₄(I), 300°C, 60 atm (or 1. conc H₂SO₄ 2. H₂O, warm)
 - Step 4: KMnO₄, H₂SO₄(aq), heat
- (c) Nucleophilic substitution



(d) (i)



(ii)







5(a)



