## 1 (a) (i)



Across the period, the atomic number increases, increasing nuclear charge. Hence, ionic radii of isoelectronic ions decrease from Na<sup>+</sup> to Si<sup>4+</sup>, and from P<sup>3-</sup> to Cl<sup>-</sup>.

The **ions of Na, Mg, Al and Si loses electrons to form cations** of one isoelectronic group containing 10 electrons, while the **ions of P, S and Cl gains electrons in the outermost valence shell to form anions** of another isoelectronic group containing 18 electrons.

Between the two isoelectronic groups, the cations have smaller ionic radii than the anions as there is <u>one less quantum shell of electrons</u>.

[4]

(ii) 
$$AlCl_3(s) + 6H_2O(I) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^{-}(aq)$$
  
 $[Al(H_2O)_6]^{3+}(aq) + H_2O(I) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}(aq)$   
 $PCl_3(I) + 3H_2O(I) \rightarrow H_3PO_3(aq) + 3HCl(aq)$   
 $Or PCl_5(s) + 4H_2O(I) \rightarrow H_3PO_4(aq) + 5HCl(aq)$ 
[2]

(b) (i)  $Ca(OH)_2(aq) + 2HCO(aq) \rightarrow Ca(CO)_2(aq) + 2H_2O(l)$  [1]

(ii) 
$$pH = pK_a + log \frac{[C/O^-]}{[HC/O]}$$
  
 $7.6 = -log(3.5 \times 10^{-8}) + log \frac{[C/O^-]}{[HC/O]}$   
 $\frac{[C/O^-]}{[HC/O]} = 1.39$ 

Amount of Ca(OH)<sub>2</sub> added =  $\frac{56.0}{74.1}$  = 0.7557 mol

Amount of  $OH^- = 0.7557 \times 2 = 1.511$  mol

Let the amount of HClO present = x when freshly treated.

	Ca(OH) <sub>2</sub>	+	2HC <i>l</i> O	$\rightarrow$	Ca(C <i>l</i> O)	+	2H <sub>2</sub> O
Initial amt / mol	0.7557		х		0		_
Change in amt / mol	-0.7557		-1.511		+0.7557		_
Eqm amt / mol	0		x–1.511		0.7557		_

$$Ca(ClO)_2 \equiv 2ClO^-$$

$$\frac{[C/O^{-}]}{[HC/O]} = \frac{\frac{2 \times 0.7557}{V}}{\frac{X - 1.511}{V}} = 1.39$$

x = 2.598 mol  
[HC/O] = 
$$\frac{2.598}{2500 \times 1000} = \frac{1.04 \times 10^{-6} \text{ mol dm}^{-3}}{2500 \times 1000}$$

[2]

(c)	(i)	PbC <i>l</i> ₂(s) ≓	Pb <sup>2+</sup>	+	2C/

Eqm conc /  $2.45 \times 10^{-2} \qquad 2 \times 2.45 \times 10^{-2} \\ \mbox{mol dm}^{-3}$ 

$$K_{sp} = [Pb^{2+}][C\Gamma]^2$$
  
= (2.45 × 10<sup>-2</sup>)(2 × 2.45 × 10<sup>-2</sup>)<sup>2</sup>  
= 5.88 × 10<sup>-5</sup> mol<sup>3</sup> dm<sup>-9</sup>

(ii) Maximum [C/] in water =  $\frac{250 \times 10^{-3}}{35.5} = \frac{7.04 \times 10^{-3} \text{ mol dm}^{-3}}{1000 \text{ mol m}^{-3}}$ 

Precipitation will occur when  $I.P > K_{sp}$ 

I.P. =  $[Pb^{2+}][C\Gamma]^2$ =  $[Pb^{2+}] (7.04 \times 10^{-3})^2 = 5.88 \times 10^{-5} \text{ mol dm}^{-3}$  $[Pb^{2+}] = 1.19 \text{ mol dm}^{-3}$ =  $2.45 \times 10^2 \text{ g dm}^{-3}$ 

Minimum mass of Pb required for a 50 cm<sup>3</sup> sample

$$= 2.45 \times 10^2 \times \frac{50}{1000}$$
$$= 12.3 g$$

(d) <u>C:H is approximately 1:1</u> ⇒ M contains a <u>benzene ring</u>

**M** reacts with ferric chloride to give purple solution  $\Rightarrow$  **M** contains a **phenol** group

**M** undergoes <u>oxidation</u> with hot acidified  $K_2Cr_2O_7$  with no  $CO_2$  evolved to give **N**  $\Rightarrow$  **M** contains an <u>alcohol</u>

**N** undergoes <u>nucleophilic substitution</u> with 1 mol of phosphorus chloride to give  $P \Rightarrow N$  contains a <u>carboxylic acid</u>, P is an <u>acyl</u> <u>chloride</u>, M is a primary alcohol.

**P** undergoes <u>acid-metal reaction</u> with sodium, and (intramolecular) <u>condensation</u>  $\Rightarrow$  **Q** contains an <u>ester</u>

(OR Q is neutral with 2 O atoms  $\Rightarrow$  Q contains an <u>ester</u>)



M:





[8]

[Total: 20]

2. (a)  

$$pV = nRT$$

$$n = \frac{(20 \times 101000)(2.20 \times 10^{-3})}{(8.31)(273 + 450)}$$

$$n = 0.740 \text{ mol}$$
[1]

(b) At 450°C, NH<sub>3</sub> has higher <u>kinetic energy</u> and is able to <u>overcome</u> <u>intermolecular forces of attraction/ Hydrogen bonds</u> between NH<sub>3</sub> molecules. <u>Hydrogen bonding/ IMF</u> between molecules becomes <u>negligible</u> and NH<sub>3</sub> behaves more like an ideal gas. [2]

(c) (i) 
$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$$
  
 $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$  [2]

(ii)  $\Delta G = \Delta H - T \Delta S$ 

Process (2) has <u>negative entropy change since number of moles</u> of gas decrease from 3 to 1.  $(-T\Delta S)$  is positive and a lower temperature will result in a more negative  $\Delta G$ . [2]

(iii)  

$$-52.2$$

$$NH_{3}(aq) + HNO_{3}(aq) \rightarrow NH_{4}NO_{3}(aq)$$

$$(-80.8) + (-207)$$

$$x$$

$$N_{2}(g) + 2H_{2}(g) + 3/2O_{2}(g)$$

$$x = (-80.8) + (-207) + (-52.2)$$

$$x = -340 \text{ kJ mol}^{-1}$$
[2]

(d) Step 1:

 $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+ [1]$ Step 2:



- (e) Ammonia is a <u>stronger base compared to phenylamine[\*]</u>. The lone pair of electron <u>on N atom in phenylamine is delocalized into the benzene ring[\*]</u>, and is <u>less available for protonation[\*]</u> compared to the lone pair of electron on ammonia.
- (f) (i) It is the regular coils and foles on a localised segment of the polypeptide strand that is stabilised by hydrogen bonds between NH and –CO group on the polypeptide backbone.







[Total: 20]

[2]

[1]

[3]

**3.** (a) (i) The order of reaction with respect to a reactant is defined as the power to which the concentration of a reactant is raised to in the experimentally-determined rate equation.

OR

The <u>overall</u> order of reaction is defined as the <u>sum of the powers</u> to which the <u>concentrations of reactants</u> are raised to in the <u>experimentally-determined rate equation</u>.

(ii)

Expt No.	Time / min	Relative rate / mol dm <sup>-3</sup> min <sup>-1</sup>
1	1.00	1.00
2	1.20	0.833
3	1.20	0.833
4	0.96	1.04

Comparing experiments <u>1 and 2</u>,

When [CN<sup>-</sup>] is increased to 1.2 times while [(CH<sub>3</sub>)<sub>2</sub>C=O] and [H<sup>+</sup>] are kept constant, rate increases to 1.2 times. Hence, order of reaction with respect to CN<sup>-</sup> is <u>1</u>.

Comparing experiments 2 and 3,

When  $[H^+]$  is increased to 1.2 times while  $[(CH_3)_2C=O]$  and  $[CN^-]$  are kept constant, rate does not change. Hence, order of reaction with respect to H<sup>+</sup> is <u>0</u>.

Comparing experiments 2 and 4,

When  $[(CH_3)_2C=O]$  is increased to 1.25 times while and  $[H^+]$  and  $[CN^-]$  are kept constant, rate increases to 1.25 times. Hence, order of reaction with respect to  $(CH_3)_2C=O$  is 1. [3]



[1]

[1]

(v)



At a higher temperature, there is a larger number of reactant particles with energy greater than or equal to the activation energy, resulting in an increase in the frequency of effective collisions between the reactant particles and hence an increased rate of reaction.

[3]



(c)	<i>(</i> i)	$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$					
(0)	(1)	Initial conc/ mol dm <sup>-3</sup>	0.200	0	0		
		Change in conc/ mol dm <sup>-3</sup>	—X	+x	+x		
		Eqm conc/ mol dm <sup>-3</sup>	0.200 - x	х	х		
		$K_{\rm a} = 10^{-4.19}$					
		$K_{a} = 6.46 \times 10^{-5}$					
		$K_{a} = x^{2} / 0.200 - x$					
		Assume that $0.200 - x \approx 0.200$	Э,				
		$x^2 / 0.200 = 6.46 \times 10^{-5}$					
		$x = [H^+] = 3.59 \times 10^{-3} \text{ mol dm}^-$	-3				
		$pH = -lg (3.59 \times 10^{-3})$					
		= 2.44				[3]	
	(ii)	$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5CO^-$	OOH + OH⁻			[1]	



4 (a) Option B [1]

Amount of  $LiNO_3 = 3.00 \times 0.95 \times 1/Mr = 0.04136 mol$ Amount of gas =  $5/4 \times 0.0414 = 0.0517 mol$ Volume of gas =  $0.0517 \times 24000 = 1240 \text{ cm}^3$  [3]

(b) Be<sup>2+</sup> is smaller and more positively-charged than Li<sup>+</sup>.

Hence, Be<sup>2+</sup> has a <u>higher charge density</u> than Li<sup>+</sup>.

Therefore,  $Be^{2+}$  has a greater polarising power and <u>weakens the N–O</u> bonds in the NO<sub>3</sub><sup>-</sup> anion to a greater extent.

Therefore,  $Be(NO_3)_2$  has a <u>lower</u> thermal decomposition temperature. [3]

(c) In the presence of ligands, the set of degenerate 3d orbitals of transition metal is split into 2 groups with different energy with a small energy gap.



complex

• d electrons from the <u>lower energy level can be promoted to the</u> <u>higher energy level</u> by absorbing a <u>certain wavelength of light from</u> <u>the visible region</u> of the electromagnetic spectrum.

The <u>colour absorbed is yellow</u> which is <u>complementary of purple</u>. [3]

(d)	(i)		Cr	S	Ν	
		Mols	0.298	1.19	2.09	
		Ratio	1	4		
		x + y ·	+ 1 = 7			
		<i>x</i> : 4	<i>y</i> : 2		[	3]
	<b>(ii)</b> +3				[	[1]

- (e) (i) A species with at least one lone pair of electrons that can form a dative bond to a central metal ion. [1]
  - (ii) Nucleophilic substitution



[1]

5. (a) (i) KC/: white fumes evolved

KBr: Mainly white fumes with some red-brown fumes

Both potassium halides (KX) react with conc sulfuric acid to form <u>hydrogen halides(HX)</u> which is the <u>white fumes</u> observed.

$$KX(s) + H_2SO_4(I) \rightarrow HX(g) + KHSO_4(s)$$
 X: C/, Br

HBr reduces  $H_2SO_4$  to  $SO_2$ , itself is oxidized to  $\underline{Br_2}$ , a red-brown fumes,

$$2HBr(g) + H_2SO_4(I) \rightarrow SO_2(g) + Br_2(g) + 2 H_2O(I)$$
[4]

(ii) Strength as reducing agent: HI > HBr > HCl
 Concentrated sulfuric acid will oxidize most of the HI produced to I<sub>2</sub>.

$$8HI (g) + H_2SO_4(I) \rightarrow H_2S(g) + 4I_2(g) + 4H_2O(I)$$
[2]

**(b)** (i) 
$$O_2 + 2 H_2O + 4e \rightleftharpoons 4 OH^- (aq) +0.40V$$

 $E_{cell}^{,}$  = +0.40 - (+1.50) = -1.1 V

The value of E<sub>cell</sub> is negative, indicating that the oxidation of gold by oxygen in the air to +3 oxidation state is not feasible [1]

(ii)  $Au(s) + NO_3^{-}(aq) + 4H^{+}(aq) + 4Cl^{-}(aq) \rightarrow AuCl_4^{-}(aq) + NO(g) + 2H_2O(l)$  [1]

(iii) 
$$Au(s) + NO_3^{-}(aq) + 4H^+(aq) + 4Cl^-(aq)$$

 $\rightarrow$  AuCl<sub>4</sub><sup>-</sup>(aq) + NO(g) + 2H<sub>2</sub>O(I)

[1]

[3]

 $E_{cell}^{i} = +0.96 - (+1.00) = -0.04V$ 

(iv) When concentrated nitric acid is used, equilibrium position of  $NO_3^-(aq) + 4H^+(aq) + 3e \Rightarrow NO(g) + 2H_2O$  (I) lies more to the right, giving rise to a more positive  $E_{red}(NO_3^-(aq)/NO(g))$ .

When concentrated hydrochloric acid is used, equilibrium position of  $AuC_{I_4}(aq) + 3e = Au(s) + 4 C_{I_4}(aq)$  lies more to the left, giving rise to less positive  $E_{red}(AuC_{I_4}(aq)/Au(s))$ .

Since  $E_{cell} = E_{red}(NO_3^{-}(aq)/NO(g)) - E_{red}(AuC/_4^{-}(aq)/Au(s)) > 0V$  when aqua regia is used, the reaction becomes feasible and gold dissolved.

(v) Dilute hydrogen peroxide or any RA with  $E_{red}^{,} < +1.00V$ 

<u>Slowly add</u>  $AuCl_4^-(aq)$ -aqua regia mixture to <u>excess</u> dilute hydrogen peroxide in an <u>ice bath</u>.  $AuCl_4^-(aq)$  will be reduced to Au(s). Filter to collect Au(s) as residue.

(c) (i) Methanol (Weakest acid). It has electron donating  $CH_3$  group to intensify the negative charge on O atom of  $CH_3O^-$ .

The negative charge on the O atom of phenoxide can be delocalized into the benzene ring, giving this anion greater stability compared to  $CH_3O^-$ .

Methanoic acid (strongest acid). The negative charge on the O atom of HCOO<sup>-</sup> can be delocalized more effectively over the COO<sup>-</sup> than in phenoxide due to its resonance structure.

(ii)



Structure of chlorate anion

 $HC/O_3$  is a stronger acid compared to methanoic acid. The negative charge on the O atom of  $C/O_3^-$  can be delocalized over to more oxygen atoms.

[Total: 20]

[3]