SAJC	2012	Prelims	P2 Solutions

Experiment	Observation	Deductions with relevant equation
Add ½ spatula of solid potassium carbonate to each separate samples (1 cm ₃) of the 4 solutions in	Effervescence OR gas evolved.	$A/(H_2O)_6^{3^+}(aq) \leftrightarrow$ $A/[(OH)(H_2O)_5]^{2^+}(aq) +$ $H_+(aq)$ $2H^+(aq) + CO_3^{2^-}(aq) →$ $H_2O(l) + CO_2(g)$
tubes.		A/Br₃ identified
	White precipitate formed	ZnCO3, Ag2CO3, CaCO3
Add each unknown sample to 1 cm ³ of A/Br ₃	No precipitate formed	ZnSO4 identified
solution till excess in clean, dry test tubes	Off-white precipitate formed	Ag₊(aq) + Br₋(aq) → AgBr(s)
ary test tubes.		AgNO₃ identified
	White precipitate formed	A <i>l</i> ₃+(aq) + 3 OH₋(aq) → A <i>l</i> (OH)₃(s)
	White ppt soluble in excess	Al(OH)₃(s) + OH₋(aq) →
		Al(OH)₄ [−] (aq)
		Ba(OH)2 identified
Add Ba(OH) ₂ dropwise till excess to 1 cm ₃ of the last unknown	White precipitate formed	Ba ²⁺ (aq) + SO₄ ^{2–} (aq) → BaSO₄(s) ZnSO₄ identified
	Experiment Add ½ spatula of solid potassium carbonate to each separate samples (1 cm ₃) of the 4 solutions in clean, dry test tubes. Add each unknown sample to 1 cm ³ of A/Br ₃ solution till excess in clean, dry test tubes. Add Ba(OH) ² dropwise till excess to 1 cm ₃ of the last unknown solution	ExperimentObservationAdd ½ spatula of solid potassium carbonate to each separate samples (1 cm3) of the 4 solutions in clean, dry test tubes.Effervescence OR gas evolved.Add each unknown sample to 1 cm³ of A/Br3 solution till excess in clean, dry test tubes.White precipitate formedOff-white precipitate formedOff-white precipitate formedWhite precipitate formedWhite precipitate formedAdd each unknown sample to 1 cm³ of A/Br3 solution till excess in clean, dry test tubes.White precipitate formedWhite precipitate formedWhite precipitate formedWhite precipitate formedWhite precipitate formedWhite precipitate formedWhite precipitate formedAdd Ba(OH)2 dropwise till excess to 1 cm3 of the last unknown solutionWhite precipitate formed

1

2(a)	(i)	The iron ion has incompletely filled d-orbitals.				
		In the isolated gas phase atoms, all 5 d orbitals of the iron ion are degenerate				
		In forming complexes, the d orbitals split into 2 groups with a small energy gap between them.				
		When a d-electron from the lower energy group is promoted to the higher energy group, energy from the visible region is absorbed.				
		The light energy not absorbed will be seen as the colour of the complex.				
	(ii)	The melting point of iron is significantly higher than that of calcium due to				
		the stronger metallic bonding present in iron and thus more energy needed				
		which is attributed to the following reasons:				
		- more delocalised electrons contributed from 3d and 4s electrons				
		- higher charge density				
	(iii)	$Fe^{3+} + e \implies Fe^{2+} +0.77V$				
		$MnO_2 + 4H^+ + 2e$ \longrightarrow $Mn^{2+} + H_2O$ $+1.23V$				
		Ag metal				
		Student can choose any reducing agent as long as the electrode potential is				
		+0.77V < x < +1.23V.				
		OR student show calculation of Ecell				
		Ecell >0 for Ag/MnO ₂ .				
		Ecell = $1.23-0.80 = +0.43V > 0$ reaction is feasible.				
		Ecell of Ag/Ee ³⁺ < 0V no reaction Ag only reduces MnO ₂				
		Ecell = $0.77 - 0.80$				
		$= -0.03 \vee < 0$				
2(b)	(i)	$CO + HCI + FeCl_3 à + CHO + FeCl_4$				
	(ii)	FeCl ₃ will hydrolyse with water to yield $[Fe(H_2O)_5(OH)]^{2+}$ and Cl ⁻ ions. OR				
		dissolve in water to form $[Fe(H_2O)_6]^{3+}$. Fe in $[Fe(H_2O)_5(OH)]^{2+}$ or Fe in				
		$[Fe(H_2O)_6]^{3+}$ has no vacant d-orbitals to accept electron pair from Cl ⁻ to				
		generate the electrophile.				
		J				



	(iii)	Benzyl radical $C_6H_5CH_2^{\bullet}$ is less stable than its reactant, $\Delta H_f C_6H_5CH_2^{\bullet}(g)$ is	
		endothermic. The radical is very reactive as it requires only 1 more electron	
		to form a stable configuration.	
		[Total mark	s : 21]
3(a)	(i)	$ \begin{bmatrix} C_{2}O_{4}^{2} - \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots \\ \vdots & \vdots \\ \vdots & \vdots \\ \vdots & \vdots \\ \vdots & \vdots &$	
	(ii)	Coordination no: 6	
3(b)	(i)	$Cl_2 + 2e \implies 2Cl^2 \qquad +1.36V$	
		$M_{\rm PO}^{-}$ + 8H ⁺ + 5e \longrightarrow Mn ²⁺ + 4H O = +1.52V	
		MnO_4^- is able to oxidise Cl^- to Cl_2 . Ecell = +0.16V, reaction is feasible.	
	(11)	Hence more MnO ₄ ⁻ will be used for the titration.	
	(ii)	When temperature is increased, the molecules gain kinetic energy and move	
		about faster. This increases the number of molecules having energy $E \ge E_A$.	
- (1)	(111)	Thus, the frequency of effective collisions increases. Reaction rate increases.	
3(b)	(111)	Calculation of % weight of $C_2O_4^2$ ion Al complex	
		$H^{+} + 2 CO_2 + 2 C \Rightarrow H_2 C_2 O_4$	
		$MnO_4^- + 8H^+ + 5e \implies Mn^{2+} + 4H_2O$ $5H_2C_2O_4 \equiv 2MnO_4^-$	
		Amt of $MnO_4^- = 27.50/1000 \times 0.0213 = 5.86 \times 10^{-4} \text{ mol}$	
		Amt of $H_2C_2O_4$ in 25 ml = 5.86 x 10 ⁻⁴ x 5/2 = 1.466 x 10 ⁻³ mol	
		Amt of $H_2C_2O_4$ in 250 ml = 1.466 x 10 ⁻³ x 10 = 1.466 x 10 ⁻² mol	
		Mass $C_2O_4^{2-} = 1.466 \times 10^{-2} \times 88.0 = 1.29 \text{ g}$	
		% of $C_2O_4^{2-}$ in complex = 1.29/1.77 x 100% = 72.9%	
	(iv)	If n =2, $K[Al(C_2O_4)_2]$	
		% of $C_2O_4^{2-}$ in complex = 176/242.1 x 100% = 72.7%	
		If n =3, K ₃ [A <i>l</i> (C ₂ O ₄) ₃]	
		% of $C_2O_4^{2-}$ in complex = 264/408.3 x 100% = 64.7%	
		Since the value obtained is closer to $n = 2$, the complex is $K[AI(C_2O_4)_2]$	
3(c)	(i)	Due to the presence of different ligand, the d orbitals are split to different extent/ energy gap, DE.	
		Rank of the d-orbital splitting $NH_3 > H_2O > F^-$	

	(ii)	Since EDTA is able to displace H ₂ O, hence it will form a stronger dative bond			
		to Co^{2+} . Hence, ΔH is negative.			
		ΔS is positive as there is an increase in entropy due to more molecules at the			
		product side, 7 molecules vs 2 molecules.			
		Using $\Delta G = \Delta H - T\Delta S$, Since $\Delta S > 0$ and ΔH is <0,			
		-T Δ S would always be <0 Δ G would be always <0 at all temperature.			
		ITotal marks:1	161		
4(a)	(i)	Nucleophilic addition			
.(a)	(ii)	OH will react with ethanol to generate a stronger nucleophile CH_2CH_2O			
	(1)				
	(11)	Nucleophilic addition			
		CH3 CHOH + OH -> CH3CH20 + H20			
		an and the CHACHE of the Ht			
		CH3 CH2OH = CIBCH2 O T H			
		- CH2CH3 8+ 8-			
		$\langle \downarrow \downarrow 0 \downarrow \neg \downarrow 0 \downarrow 1 \downarrow 0 CH2CH2$			
		CH3CH2Ö- fast			
		OCH2CH3 + CH3CH2O-			
		Generation of Nucleophile			
		· Slow			
		Intermediate			
		Arrow Partial charges + lone pair			
	(iv)	OH OH OCH_2CH_3			
		H			
		OCH ₂ CH ₃ H ⁺ catal.st			
		An Acetal			
		Calcium chloride is a drving agent, which help to remove water. Hence the			
		position equilibrium will shift right to increase the yield of the product.			
4(b)	(i)				
	(')	Percentage by 51.2 7.7 13.7 27.4			
		mass / %			
		Simplest ratio 5 9 1 1			
		Empirical formula = C_5H_9OS			

