2854/01 Chemistry by Design

June 2003

Mark Scheme

The following annotations may be used when marking:

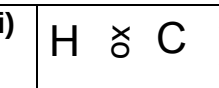
X	=	incorrect response (errors may also be underlined)
^	=	omission mark
bod	=	benefit of the doubt (where professional judgement has been used)
ecf	=	error carried forward (in consequential marking)
con	=	contradiction (in cases where candidates contradict themselves in the same response)
sf	=	error in the number of significant figures

Abbreviations, annotations and conventions used in the Mark Scheme:

/	=	alternative and acceptable answers for the same marking point
;	=	separates marking points
NOT	=	answers not worthy of credit
( )	=	words which are not essential to gain credit
___ (underlining)	=	key words which must be used
ecf	=	allow error carried forward in consequential marking
AW	=	alternative wording
ora	=	or reverse argument

1	**(a)**	**(i)**	Crude oil / oil/ petroleum (oil);	1
		(ii)	Impurity binds to / bonds to / attaches to / reacts with / is adsorbed on catalyst surface; (not absorbed) prevents reactants reaching catalyst surface / blocks active sites/reduces active area/makes catalyst inactive (or wtte);	2
	(b)		Surface / active area of the catalyst; is reduced;	2
	(c)	**(i)**	Formation of methanol / forward reaction is exothermic; Cooling shifts equilibrium in favour / direction of the exothermic change; (thus) increasing the yield; (or reverse argument)	3
		(ii)	Kp = $\frac{pCH_3OH \times pH_2O}{pCO_2 \times pH_2^3}$ (1 for top; 1 for bottom;) (Wrong way up OR square brackets [even if Kp used] scores 1) (correct expression for *equation 1.1* scores 1)	2
		(iii)	Higher yield / shifts equilibrium to the right; faster / higher rate;	2
		(iv)	Lower energy requirements/high pressure costly to create or maintain/stronger plant required/thick-walled pipes or plant required/more health and safety systems required;	1
	(d)	**(i)**	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ correct equation; correct state symbols;	2
		(ii)	25-250 atm; 400 to 500 ^oC / 650K to 800K; iron or rhenium catalyst; (allow any temperature range within the stated range)	3
	(e)		$2KHCO_3(aq) \rightarrow K_2CO_3(aq) + H_2O(l) + CO_2(g)$ formulae of reactant and products correct; balanced; (ignore state symbols)	2

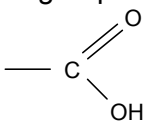
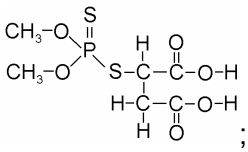
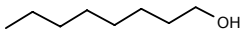
[Total: 20]

2	**(a)**	**(i)**	 triple bond; rest of molecule; (allow same symbol [o or x] throughout)	2
		(ii)	Two regions of electrons / electron density / negative charge / bonds around each carbon atom; repel as far apart as possible / to a position where minimum repulsion exists / get as far away from each other as possible;	2
	(b)	**(i)**	Electrons are not localised / located / placed between / bonded to / fixed between / (all) carbon atoms (stated or implied); spread out (evenly) / free to move along the carbon chain / between carbon atoms;	2
		(ii)	**Ignore everything outside visible spectrum** Maximum absorption in red-orange region :- 2 marks some absorption in the red-orange region :- 1 mark	2
		(iii)	**NO CHOICE POINTS:** reference to energy levels / energy states; electrons need/absorb energy/light to be excited/to move to higher energy levels; absorbed from visible light / radiation in visible spectrum; complementary colour transmitted/reflected; (emitted disqualifies this mark) (allow "if blue absorbed, red reflected" or reverse argument) **THEN 2 FROM:** absorption in visible region because excitation energy in poly(ethyne) is low; difference in energy gap (between cis and trans forms); cis form has greater gap / excitation energy of cis form is higher; (greater gap corresponds to) blue light/radiation or light of higher energy/frequency/lower wavelength; (or reverse argument)	6
	(c)		**EITHER:** add functional group / side chain; example (eg NH_2, OH, SO_3H) / to change the conjugation **OR:** add more double bonds; to extend the conjugation/conjugated system; **OR:** change orientation of benzene ring/position of side chains; to 1:2 or 1:3; **OR:** change configuration of C=C; to make the cis form; (**NB:** two first 'general points' can gain 2 marks)	2

[Total: 16]

3	**(a)**		Ca^{2+}; surrounded by at least 3 water molecules; at least one water molecule showing oxygen carrying δ-; δ- /oxygen adjacent to the metal ion; (representation of water molecule by a triangle allowed provided a key is added, showing what it represents : no key but δ- shown in correct place loses the third marking point)	4
	(b)	**(i)**	calcium ion has the higher charge density;; (ie 2 marks) OR small ion; high charge;	2
		(ii)	hydrated ion is bigger because it has more water molecules in it; hydrated ion has lower charge density;	2
	(c)	**(i)**	Ammonium ions attracted to the negatively-charged clay / soil; nitrate ions are negatively charged / are repelled by the clay;	2
		(ii)	-3; +5; (a sign is essential) (3- and 5+ earns one mark)	2
		(iii)	Hydrogen ions / protons released/formed; H^+ causes acidicity / acid is proton donor; H_3O^+ is more acidic than NH_4^+ earns 2 marks	2
		(iv)	**2 from:** higher concentration of $H^+(aq)$; hydrogen ions displace calcium ions; hydrogen ions have a greater affinity for the clay;	2
	(d)		products: all of Ca^{2+}, H_2O, CO_2 and no other component; balanced: $CaCO_3(s) + 2H_3O^+ \rightarrow Ca^{2+}(aq) + 3H_2O(l) + CO_2(g)$; state symbols; (allow state symbol mark if equation is wrong but substances are 'real')	3
	(e)	**(i)**	pH = -log[H^+(aq)] (stated or implied); pH = 6 - log 2.5 / 0.4 = 5.6; (allow 5.6 or 5.60 or 5.602)	2
		(ii)	SOx / SO_2 / NOx / NO_2 / H_2SO_4 ; more dissolved;	2

[Total: 23]

4	(a)	(i)	**Compound A**: one carboxylic acid group shown:  CO_2H / COOH / CO_2^- and appropriate cation; rest correct, ie  **Compound B:** C_2H_5OH / $CH_3.CH_2.OH$ / full structural formula;	3
		(ii)	Ethanol; (allow ecf from (a)(i))	1
		(iii)	Reflux; with aqueous or dilute or moderately concentrated acid / H^+ / OH^- / alkali / H_2SO_4 / HCl / H_3PO_4 / NaOH / Na_2CO_3	2
	(b)		**NO CHOICE POINTS:** water molecules linked by hydrogen bonds/IMF in water are hydrogen bonds; hydrogen bonds are strong; octan-1-ol forms weaker IMF with water; IMF between octan-1-ol and water not sufficiently strong to overcome IMF/hydrogen bonds between water molecules; **AND THREE FROM:** structure / formula of octan-1-ol: $C_8H_{17}OH$ /  / full structural formula; hydrogen bonds are formed between O in one molecule and H in another; hydrogen bonds are formed because of the difference of electronegativity between hydrogen and oxygen; octan-1-ol is less polar than water; an effect of carbon chain; **QWC** for scientific and technical terms: at least two complete sentences containing TWO of polar, intermolecular forces, hydrogen bonds, electronegativity	7 + 1
	(c)		Parathion more soluble in octan-1-ol than in water; because it cannot form strong hydrogen bonds with water / can form id-id or pd-pd intermolecular forces with octan-1-ol OR because Parathion is more soluble in fats OR octan-1-ol has low polarity or is non-polar; (Thus) concentration of Parathion in octan-1-ol is greater than the concentration in water;	3

[Total: 17]

5	**(a)**	**(i)**	Number of moles of Ag^+ = $\frac{24.7}{1000}$ x 0.05 = 1.235×10^{-3} or 1.24×10^{-3}	1
		(ii)	Number of moles of NaCl ≡ Number of moles of Ag^+ = 1.235×10^{-3} (allow ecf)	1
		(iii)	Moles of chloride ion in 1 dm^3 = $1.235 \times 10^{-3}/0.01$ = 0.1235; (ecf applies) Concentration = 0.1235 x 35.5; = 4.38 g dm^{-3}; (sig fig rule to apply) (accept 4.40 if (a)(i) is 1.24×10^{-3}) (4.4 :- 2 max) (if (a)(i) gives 1.2×10^{-3}, 4.3 is necessary to earn the sig fig mark) (even if wrong answer shown but if sig fig correct - 1 mark)	3
	(b)	**(i)**	$K_{sp} = [Ag^+][Cl^-]$; (penalise wrong state symbols)	1
		(ii)	Concentration of Ag^+ = $\frac{0.1 \times 0.01}{0.2}$ = 5×10^{-3} (mol dm^{-3}); Concentration of Cl^- = $\frac{0.1 \times 0.001}{0.2}$ = 5×10^{-4} (mol dm^{-3}); [Ag+] x $[Cl^-] = 2.5 \times 10^{-6}$; which is greater than K_{sp} Therefore a precipitate formed; (has to be a reason to gain this mark : ecf can apply)	4
	(c)	**(i)**	(aq) and (aq) → (s) and (aq) / a solid is formed; system becomes more ordered / solid has lower entropy / decrease in entropy / solid is more ordered;	2
		(ii)	Reaction spontaneous / "goes" / takes place; hence ΔS_{total} must be positive; Therefore ΔS_{surr} must be positive because ΔS_{sys} is negative;	3

[Total: 15]

6	**(a)**	**(i)**	**3 from:** ester; ether / methoxy-; alkene; arene / benzene ring;	3
		(ii)	Eugenol has a phenol / phenolic -OH group; add (neutral) iron(III) chloride solution / acid-base indicator; turns purple / takes up the acidic colour;	3
		(iii)	**EITHER:** (Anhydrous) ethanoyl chloride; room temperature; **OR:** ethanoic anhydride; reflux with concentrated sulphuric acid;	2
		(iv)	Esterification / condensation / nucleophilic substitution / acylation / ethanoylation;	1
	(b)		**5 from:** vanillin is more soluble in hot water than cold; vanillin crystallises when the hot solution cools; because the solution becomes saturated / amount / concentration in solution exceeds the solubility; impurities remain in solution or can be filtered; vanillin is highly soluble in ethanol at both high and low temperatures / at all temperatures; would not crystallise on cooling; **QWC** for spelling, grammar and punctuation: at least TWO complete and relevant sentences containing NO MORE THAN ONE spelling, punctuation or grammatical errors.	5 + 1
	(c)	**(i)**	Structural / position(al) isomerism;	1
		(ii)	Molecule of Y has a different shape; does not fit the same receptor / fits different receptors / active sites;	2
		(iii)	distillation / chromatography / fractional crystallisation / molecular sieve; (NOT crystallisation)	1
	(d)	**(i)**	**7 points for vanillin (ora):** (**6 max** if appropriate arguments applied to wrong compound) vanillin contains aldehyde group; **infra-red :** vanillin shows a peak at 1680-1750/1670-1690; because of C=O bond; **nmr:** peak at 10/9.8/9.7 (NOT 9.5); due to proton/hydrogen in CHO group; proton ratio in vanillin is 1:3:3:1 / proton ratio in guaiacol is 3:4:1; (therefore) 4 peaks in vanillin spectrum / 3 peaks in guaiacol spectrum; smaller peak at 7.2/7.5 in vanillin; due to fewer aryl hydrogens / protons; **QWC:** Logical presentation of evidence: at least two logical statements (ie of the sort *evidence, therefore conclusion*) (table/bullet points allowed);	7 + 1
		(ii)	$C_8H_8O_3$;	1
		(iii)	Molecular (ion) peak / highest mass peak at 152;	1
				[Total: 29]