Version 1.0: *08/05*

ASSESSMENT and QUALIFICATIONS ALLIANCE

Advanced Extension Award

Chemistry 6821

Mark Scheme

2005 examination - June series

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

Advanced Extension Award (AEA)

This Mark Scheme covers the Advanced Extension Award that AQA offers on behalf of all awarding bodies

Further copies of this Mark Scheme are available to download from the AQA Website: www.aqa.org.uk

Set and published by the Assessment and Qualifications Alliance.

The Assessment and Qualifications Alliance (AQA) is a company limited by guarantee registered in England and Wales 3644723 and a registered charity number 1073334. Registered address AQA, Devas Street, Manchester. M15 6EX. *Dr Michael Cresswell Director General.*

Question 1

(a)	As_4O_6 + 12NaOH → $4Na_3AsO_3$ + $6H_2O$ etc; *(allow ionic equations with $[As(OH)_4]^-$ or $[As(OH)_6]^{3-}$)*	(1)	
	As_4O_6 + 12HCl → $4AsCl_3$ + $6H_2O$ etc; *(allow ionic equations with As^{3+} or $[As(H_2O)_6]^{3+}$ and any acid)*	(1)	**2**
(b)	As_4O_6 + 12Zn + $24H^+$ → $4AsH_3$ + $6H_2O$ + $12Zn^{2+}$;	(1)	**1**
(c)	Sb has one more electron shell or larger atom or more shielding;	(1)	
	Sb - H bond is longer;	(1)	
	Sb - H bond energy less than As - H bond energy; *(CE = 0 if ions considered)*	(1)	**3**
(d)	moles thio = 18.5 × 0.050 / 1000 = 9.25×10^{-4};	(1)	
	moles AsO_4^{3-} = 9.25×10^{-4}/ 2 = 4.625×10^{-4};	(1)	
	mass As = 4.625×10^{-4} × 74.9 = 0.0346 g;	(1)	**3**

(answers must be to a minimum of 3 significant figures)
(penalise the last mark if an additional less accurate answer then given)
(max one if M2 incorrect)
(mark consequentially to AE; one mark is lost)

(e)	CH_3COO^- + $2H_2O$ → $2CO_2$ + $7H^+$ + $8e^-$;	(1)	**1**

Question 2

(a) (i) $K_p = \dfrac{pH_2 \times pO_2^{0.5}}{pH_2O}$; (1)

or shown in the calculation

Assume start with 1 mol of steam then, at equilibrium

	Moles	Mole fraction	Partial Pressure	Pp/atm	
H_2O	1-0.05	0.95/1.025 i.e. 0.927	107 kPa	1.06	(1)
H_2	0.05	0.05/1.025 i.e. 0.0488	5.61 kPa	0.556	(1)
O_2	0.025	0.025/1.025 i.e. 0.0244	2.80 kPa	0.0278	(1)

K_p = 0.088 or 0.089 (1) kPa$^{0.5}$ (1) (0.0088 atm) **6**

allow unit mark independently if K_p correct

If partial pressures not calculated allow:
Total moles *(1)*
Correct method for the calculation of mole fraction *(1)*
Correct method for the calculation of partial pressure *(1)*

If K_p inverted or wrong allow max 3 for partial pressure calculations
If calculation in Pa i.e. answer = 2.81(1) Pa $^{0.5}$ *(1)*

(ii) Reaction endothermic; (1)
K_p increases as T increases; (1)
(allow conseq to inverted K_p)
K_p unchanged with change in pressure; (1) **3**
(allow correct answers based on ΔG and $T\Delta S$)

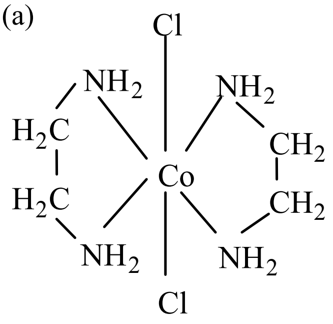
(iii) not suitable for the manufacture of hydrogen
reason e.g. yield too small,
cost *(of energy)* to generate 3000K *OR* are too high; (1) **1**

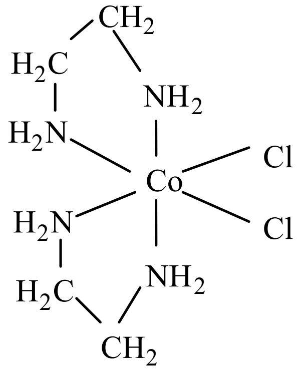
(b) (i) k_1 small hence activation energy high *OR*
k_2 larger hence activation energy low; (1)
k_1 small because covalent bond must be broken; (1)
k_2 larger because ions of opposite charge attract; (1) **3**
(mark M2 and M3 separately)

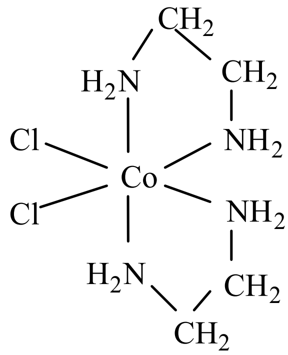
	(ii)	rate of forward = $k_1[H_2O]$; rate backward = $k_2[H^+][OH^-]$;	(1)	
		$k_1[H_2O] = k_2[H^+][OH^-]$ *or* $[H^+][OH^-]/[H_2O] = K_c$;	(1)	
		$K_c = k_1/k_2$;	(1)	
		$= 2.50 \times 10^{-5} / 1.39 \times 10^{11} = 1.80 \times 10^{-16}$ mol dm^{-3}; (1)		4
		due to possible ambiguous reading of the question allow last two marks for:		
		$[H^+][OH^-]/[H_2O] = K_c$;	(1)	
		1.80×10^{-16} mol dm^{-3};	(1)	
		(regardless of method of calculation used)	(1)	
	(iii)	K_c is constant at a fixed temperature;	(1)	
		$[H_2O]$ is approximately constant;	(1)	
		$K_w = 1.80 \times 10^{-16} \times 55.6$;	(1)	3
		(do not allow $[10^{-7}]^2$ for the last mark)		
	(iv)	% $H^+ = (1.0 \times 10^{-7} \times 100) / 55.6$;	(1)	
		Answer = 1.8×10^{-7};	(1)	2
(c)	(i)	$K_a = 1.26 \times 10^{-5}$;	(1)	
		$[H^+] = 3.55 \times 10^{-3}$;	(1)	
		% = 0.355% or 0.036 or 0.059% if all 6 water molecules are considered;	(1)	
		Al^{3+} ions polarise co-ordinated water causing either release of ions or O - H bonds weakened;	(1)	4
		note: alternative method for M1 and M2:		
		$pH = {}^1/_2 pK_a - {}^1/_2 \log [HA]$		
		$pH = {}^1/_2 pK_a = 2.45$;	(1)	
		$[H^+] = 3.55 \times 10^{-3}$ *or* 3.6×10^{-3};	(1)	
	(ii)	moles $[Al(H_2O)_5(OH)]^{2+}(aq)$ formed = moles NaOH = 0.02;	(1)	
		moles $[Al(H_2O)_6]^{3+}(aq)$ = 0.08 - 0.02 = 0.06;	(1)	
		$[H^+] = K_a \times 0.06 / 0.02 = 3.78 \times 10^{-5}$;	(1)	
		pH = 4.42;	(1)	4

Question 3

(a)







(1) (1) (1)

the bidentate ligand shown correctly bonded; (1) **4**
if a key is given, N must be shown co-ordinately bonded to Co
ignore charges
ignore duplicate structures
penalise incorrect structures; apply list principle if more than 3 given

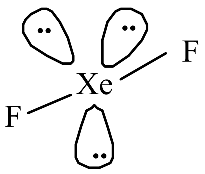
(b) (i) $F_2 \rightarrow 2F\bullet$; (1)
$Xe + F\bullet \rightarrow XeF\bullet$; (1)
$XeF\bullet + F_2 \rightarrow XeF_2 + F\bullet$ or $XeF\bullet + F\bullet \rightarrow XeF_2$; (1) **3**

do not allow ionic species
do not allow Xe•
apply list principle to propagation and termination steps

(ii) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$ (1) **1**
allow $2H_2F_2$ *or* $4H^+ + 4F^-$

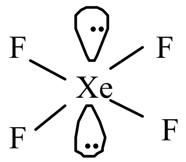
(iii) XeF_2

a diagram showing linear shape ; (1)
three lone pairs around Xe; (1)



XeF_4

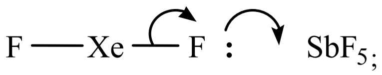
a diagram showing square planar shape; (1)
two lone pairs around Xe; (1)



XeF_5^-

a diagram with five bond and two lone pairs around Xe; (1)
bond angle = 72^o; (1) **6**
allow lone pairs shown as ●● or ×× but bonds must be lines
penalise Xe ÷ F once only
CE = 0 if number of lone pairs incorrect in XeF_2 and XeF_4

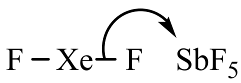
(iv) $[XeF]^+[SbF_6]^-$; (1)



(2) **3**

i.e. each correct curly arrow scores 1 mark

electron pair does not have to be shown
allow an ionic mechanism
allow max one for:



(v) $XeF_6 + 7OH^- \rightarrow HXeO_4^- + 3H_2O + 6F^-$ *or*
$XeF_6 + 4OH^- \rightarrow HXeO_4^- + 3HF + 3F^-$ *or*
$XeF_6 + OH^- + 3H_2O \rightarrow HXeO_4^- + 6HF$; (1) **1**
allow equations with H^+ and F^- in alternative answers 2 and 3

(vi) $HXeO_4^- + 7H^+ + 6e^- \rightarrow Xe + 4H_2O$; (1)

$HXeO_4^- + 2H_2O \rightarrow XeO_6^{2-} + 5H^+ + 4e^-$; (1)

$5HXeO_4^- \rightarrow 3XeO_6^{2-} + 2Xe + H^+ + 2H_2O$; (1) **3**
final equation is not marked consequentially

(c)	M1	moles $(NH_3OH)_2SO_4$ = 4.33 × 10^{-3} mol;	(1)	
	M2	moles $(NH_3OH)^+$ used in the reaction = 8.67 × 10^{-4} mol;	(1)	
	M3	moles MnO_4^- used = 3.47 × 10^{-4} mol;	(1)	
	M4	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ *or*		
		MnO_4^- : Fe^{2+} ratio = 1: 5;	(1)	
	M5	moles Fe^{2+} produced by $[NH_3OH]^+$ = 1.735 × 10^{-3} mol;	(1)	
	M6	Fe^{3+} : $(NH_3OH)^+$ ratio = 2:1;	(1)	
		each N loses 2 e^-		
	M7	oxidation states of N: in NH_2OH = -1 in nitrogen oxide = +1	(1)	
	M8	oxide = N_2O or dinitrogen oxide	(1)	
	M9	$4Fe^{3+} + 2(NH_3OH)^+ \rightarrow N_2O + 4Fe^{2+} + 6H^+ + H_2O$	(1)	**9**

if M1 wrong penalise M1, M6, M8 and M9; mark M2 and M7 consequentially
if M2 wrong penalise M2, M6, M8 and M9; mark M7 consequentially
if M3 wrong penalise M3, M6, M8 and M9; mark M5 and M7 consequentially
if M4 wrong penalise M4, M6, M8 and M9; mark M5 and M7 consequentially

Question 4

(a) (i) $Cl_2 \rightarrow 2Cl\bullet$ (1)

$CH_3CH_2CH_2CH_3 + Cl\bullet \rightarrow CH_3\dot{C}HCH_2CH_3 + HCl$ (1)

$CH_3\dot{C}HCH_2CH_3 + Cl_2 \rightarrow CH_3CH(Cl)CH_2CH_3 + Cl\bullet$ (1)

u.v. light or heat or sunlight (1) **4**

allow product formed in either a propagation or a temination step

(ii) $CH_3CH_2CH_2CH_2Cl$; (1)

Ratio 3:2 for 1-chloro : 2 chloro from ratio of H atoms; (1) **2**

the reason must be justified

(iii) The radical $CH_3\dot{C}HCH_2CH_3$ is planar around C•; (1)

Therefore attack from either side; (1) **2**

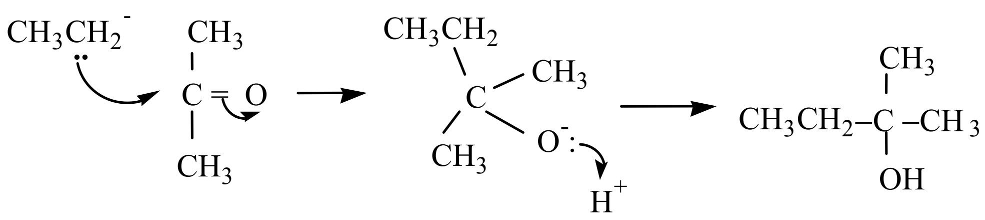
allow M2 only if M1 is given correctly

(iv) isomers are ++ and – – and + – All three given score (2)

Any two given score (1) **2**

answers must be in words

(b) (i)



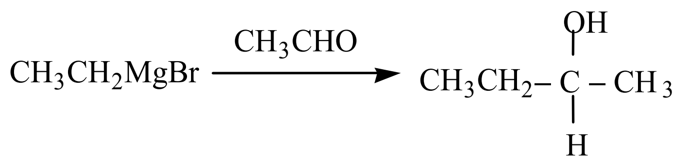
(1) (1) (1) **3**

electron pairs do not have to be shown

(ii) CH_3CH_2COOH (1) **1**

do not allow the name

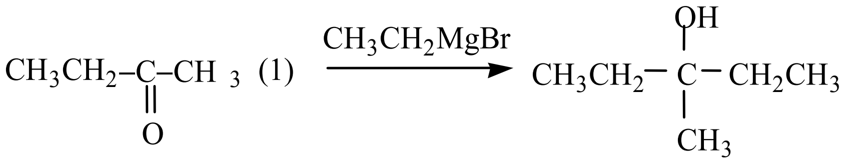
(iii)



(1)

allow name

$K_2Cr_2O_7 / H^+$ *or name but not* $KMnO_4$ (1)



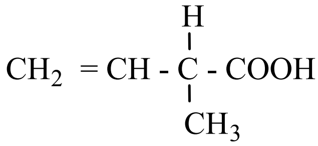
(1)

2

CE = 0 if other reagents used

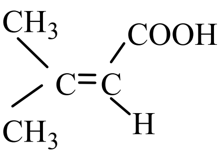
(iv) $CH_3CH_2^-$ reacts with δ+H or extracts a proton or H^+ from water *or* lone pair on H_2O donated to Mg^{2+}; (1)
CH_3CH_3; (1) **2**

(c)

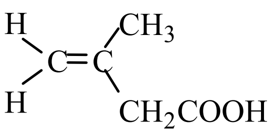
A 

(1)

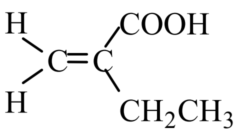
B/C/D



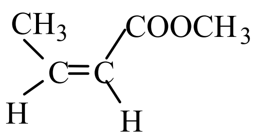
(1)



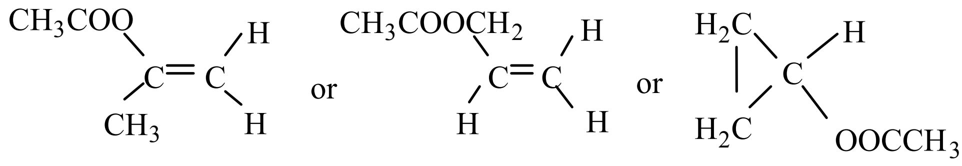
(1)

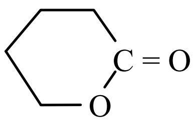


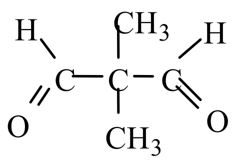
(1)

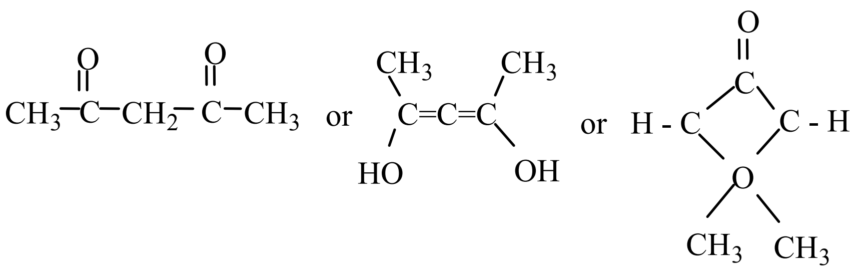
E 

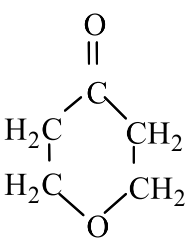
(1)

F  (1)

G  (1)

H  (1)

I  (1)

J  (1) **10**

structures A E and F must be clearly labelled

Question 5

(a)	sodium chloride and magnesium fluoride:			
	ion-ion attraction		(1)	
	the charge on Mg^{2+} is larger than that on Na^{+}		(1)	
	the radius of Mg^{2+} is smaller than that on Na^{+}		(1)	
	the radius of F^{-} smaller than Cl^{-}		(1)	
	Mg^{2+} attracts F^{-} more strongly or Na^{+} attracts Cl^{-} less strongly		(1)	**5**
	CE = 0 if type of interaction incorrect			
	diamond and silicon:			
	covalent bonds must be broken (on melting)		(1)	
	both macromolecular or giant covalent or giant molecular		(1)	
	Si larger atom than C		(1)	
	longer and weaker bonds		(1)	**4**
	CE =0 if a molecular species given			
	CE =0 if SiO_2 considered			
	1-chlorobutane and bromomethane:			
	dipole - dipole attraction		(1)	
	chlorine more electronegativity than bromine		(1)	
	C-Cl bond more polar than C - Br bond; hence bigger dipole-dipole attraction		(1)	
	van der Waals attractions		(1)	
	van der Waals attractions also larger in 1-chlorobutane as molecules are larger *or* longer *or* more temporary dipole - dipole attractions can be produced		(1)	**5**
	water and ethanol:			
	hydrogen bonding		(1)	
	water forms more hydrogen bonds than ethanol		(1)	
	van der Waals attractions		(1)	
	van der Waals attraction greater for ethanol as molecules larger *or* have more electrons		(1)	
	hydrogen bonding stronger than van der Waals attraction		(1)	**5**
			Max 17	
QWC	Correct use of technical language in not less than 2 sections	C	(1)	
	Written in sentences and all 4 sections considered	W	(1)	
	Answers presented in a logical form in not less than 3 sections	A	(1)	
			Max 3	

(b)	M1	electrophiles have a positively charged atom or seek electrons		(1)	
	M2	alkenes have high electron density between two C atoms *or* 4 electrons *or* in a π *or* in a double bond		(1)	
	M3	benzene has delocalised electrons *or* lower electron density between C atoms		(1)	
	M4	benzene less reactive *or* more stable *or* explained		(1)	
	M5	needs a positive species produced by reaction with a catalyst		(1)	
	M6	nucleophiles are negatively charged *or* are electron pair donors		(1)	
	M7	repelled by centres of high electron density		(1)	**7**
	M1	a Brønsted - Lowry acid is a proton donor		(1)	
	M2	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH3COO^-$		(1)	
	M3	NH_3 is a better proton acceptor *or* stronger base or electron pair acceptor than H_2O		(1)	
	M4	$CH_3COOH + NH_3 \rightleftharpoons NH_4{}^+ + CH_3COO^-$		(1)	
	M5	acid strength depends on equilibrium position		(1)	
	M6	equilibrium to left in water but to right in ammonia *or* a valid comparison		(1)	**6**
	M1	$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$		(1)	
	M2	$nSi(OH)_4 \rightarrow (SiO_2)n + 2nH_2O$ or in words or structures		(1)	
	M3	$(CH_3)_2SiCl_2$ initially reacts with water forming $(CH_3)_2Si(OH)_2$		(1)	
	M4	molecules condense or water eliminated between molecules		(1)	
	M5	this forms a linear polymer		(1)	
	M6	in the presence of $SiCl_4$ or $Si(OH)_4$ chains link together		(1)	**6**
				Max 17	
QWC		correct use of technical language in at least one section	C	(1)	
		written in sentences and all 3 examples considered	W	(1)	
		answers presented in a logical form in not less than 2 sections	A	(1)	
				Max 3	