Version 1.0: 0707

ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6821

AEA Chemistry

Mark Scheme

2007 examination - June series

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Question 1

(a)	$CH_3CH_2CH_2OH$ + $SOCl_2$ → SO_2 + HCl + $CH_3CH_2CH_2Cl$	(1)	
	$CH_3CH_2CH_2OH$ + PCl_5 → $POCl_3$ + HCl + $CH_3CH_2CH_2Cl$	(1)	
	($CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2Cl$ must be shown once)		
	Both other products are gases therefore fewer products to separate/ simpler purification process (*Not more economic, allow SO_2 is a gas $POCl_3$ is a liquid*)	(1)	**3**
(b)	$Co(OH)_2.4H_2O$ + $6SOCl_2$ → $CoCl_2$ + $6SO_2$ + 10HCl	(1)	**1**
(c)	$SOCl_2$ molecule has a dipole whereas SO_2Cl_2 doesn't	(1)	
	SO_2Cl_2 has larger van der Waals' forces than $SOCl_2$ since more electrons *(Allow greater M_r)*	(1)	
	Total of van der Waals' + dipole – dipole greater for $SOCl_2$ / more efficient packing / $SOCl_2$ molecules can get closer together (*If hydrogen bonding mentioned only M2 available*)	(1)	**3**
(d)	SO_2Cl_2 + $2H_2O$ → H_2SO_4 + 2HCl; *(allow ions on rhs)*		**1**
(e)	Increasing temperature pushes equilibrium to rhs/increases K_c	(1)	
	(Forward reaction is endothermic) therefore reverse reaction is exothermic	(1)	**2**
			Total 10

Question 2

(a)		$F_2 + CH_4 \rightarrow CH_3F + HF$	(1)	
		Halogen-Halogen bond must be broken / homolytic fission	(1)	
		The F–F bond is weaker than Cl–Cl	(1)	
		The activation energy for F_2 is lower /enough energy to break it at room temperature	(1)	**4**
(b)	(i)	The H–F bond is stronger than the H–Cl bond (therefore HF is less dissociated in aq solution)		**1**
	(ii)	For HF $K_a = \frac{[H^+][F^-]}{[HF]}$	(1)	
		$[H^+]^2 = 5.62 \times 10^{-4} \times 0.20$	(1)	
		$[H^+] = 1.06 \times 10^{-2}$ therefore pH = 1.98 or 2.97 (*Accept 2 or 3 decimal places only*)	(1)	
		Weak acid so assume [HF] = 0.20 or all H^+ comes from HF or $[H^+] = [F^-]$	(1)	**4**
	(iii)	$HF + NaOH \rightarrow NaF + H_2O$		
		Moles NaOH = $50/1000 \times 0.100 = 5.0 \times 10^{-3}$	(1)	
		Moles HF remaining = $100/1000 \times 0.200 - 5 \times 10^{-3} = 15.0 \times 10^{-3}$	(1)	
		$K_a = [H^+] \times 5/15$; *(if $[H^+]^2$ used or $\sqrt{K_a C}$ only M1 and M2 available)*	(1)	
		$[H^+] = 3 \times 5.62 \times 10^{-4}$ therefore pH = 2.77; (*Conseq. On M1 and M2*)	(1)	**4**
	(iv)	$H^+ + F^- \rightarrow HF$ moles F^- left = $5.00 \times 10^{-3} - 0.50 \times 10^{-3} = 4.50 \times 10^{-3}$	(1)	
		Moles HF formed plus there already = $15.0 \times 10^{-3} + 0.50 \times 10^{-3}$ = 15.50×10^{-3}	(1)	
		$K_a = [H^+] \times 4.5/15.5$ therefore $[H^+] = K_a \times 15.5/4.5$ = 1.93×10^{-3} mol dm^{-3} Therefore pH = 2.71	(1)	
		(*CE if moles of HF not calculated or if F^- not calculated as a difference*) pH remains approx constant because the solution <u>is a buffer</u> (stand alone);	(1)	**4**

(c) $K_a = \dfrac{[H^+][F^-]}{[HF]}$

assume $[F^-] = 0.50$; (1)
(*Can be given if seen in K_a relationship*)

$[OH^-] = 1 \times 10^{-14}/[H^+]$ (= [HF]) *(Correct use of K_w)* (1)

(*If first two points correct but answer wrong* check *for arithmetic error)*

$K_a = [H^+]^2 \times 0.50/10^{-14}$ (1)

$[H^+]^2 = K_a \times 10^{-14}/0.50 = 5.62 \times 10^{-18}/0.50$
$[H^+] = 3.35 \times 10^{-9}$ therefore pH = 8.47 (1) **4**

(d) ΔH = +902 – (406 + 506) (*or correct cycle*) (1)
= -10 (kJ mol^{-1}) *(Allow 1 mark for +10 kJ mol^{-1})* (1) **2**

(e) Moles NaF = 4/(23+19) = $9.5(2) \times 10^{-2}$ in 100 cm^3 (1)

$[Na^+] = [F^-] = 9.5(2) \times 10^{-1}$ (mol dm^{-3}) (1)

$K_s = 9.06 - 9.07 \times 10^{-1}$ $\underline{mol^2}$ $\underline{dm^{-6}}$ (1) **3**
(*3 sig fig for Ks*)

(f) $\log_{10}K_{333} + 4.24 \times 10^{-2} = \dfrac{10000}{(2.3 \times 8.31)} \left(\dfrac{1}{333} - \dfrac{1}{293} \right)$ (1)

$\log_{10}K_{333}$ = –0.214 – 0.0424 = –0.257 therefore $K_{333} = 0.554$ mol^2 dm^{-6} (1)

$[Na^+] = \sqrt{(0.554)} = 0.744$ mol dm^{-3} (1)

Solubility = 31.3 g NaF in 1.0 dm^3 = 3.13 g in 100 cm^3 (*Allow 3.0 – 3.2*) (1) **4**
(Max 3 if ΔH is -10 or -0.01)
(Using K_s = 1.2 mol^2 dm^{-6} and ΔH = -15 kJ mol^{-1} ans 3.1 -3.2)
(If own value K_s or ΔH mixed with 'fall back' values, calculation must be checked)

Total 30

Question 3

(a) $BaSO_4$ is very insoluble; (1)

$BaCO_3$ reacts with stomach or hydrochloric acids; (1)

Forming a solution; (1)

$BaCO_3 + 2HCl \rightarrow BaCl_2 + CO_2 + H_2O$ (1) **4**
(*Allow H_2CO_3*)

(b) (i) **B =** structural formula for $Cl_3SiOSiCl_2OSiCl_3$ showing all bonds; **1**
(*Allow any correct structure showing bonding and symmetry*)

(ii) Moles AgCl / Cl^- precipitated $= 42.1 \times 10^{-3} \times 0.0500$
$= 2.1(1) \times 10^{-3}$ mol; (1)

Moles Cl in **A** = $\frac{0.100}{285.2} \times 6 = 2.10 \times 10^{-3}$ mol hence **A** (1)

Or mass Cl = 0.075 g

Moles Cl in **B** = $\frac{0.100}{400.3} \times 8 = 2.00 \times 10^{-3}$ mol (hence not **B**) (1) **3**

Or mass Cl = 0.071 g
(*Allows answers in terms of moles or mass of Cl*)

(c) (Red) $2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$ (1)
(*Accept $6H^+ + 6\ Cl^-$*)

(Base) $NH_3 + HCl \rightarrow NH_4Cl$ (1)
(*Accept $NH_3 + H^+ \rightarrow NH_4^+$*)
$8NH_3 + 3Cl_2 \rightarrow N_2 + 6\ NH_4Cl$ (1) **3**

(d) (i) Empirical formula = $PNCl_2$ (1)

Molecular formula = $P_4N_4Cl_8$ (1)
(both must be stated)

$4PCl_5 + 4NH_4Cl \rightarrow P_4N_4Cl_8 + 16HCl$ (1)
(*If no molecular formula deduced allow empirical formula in the equation*)

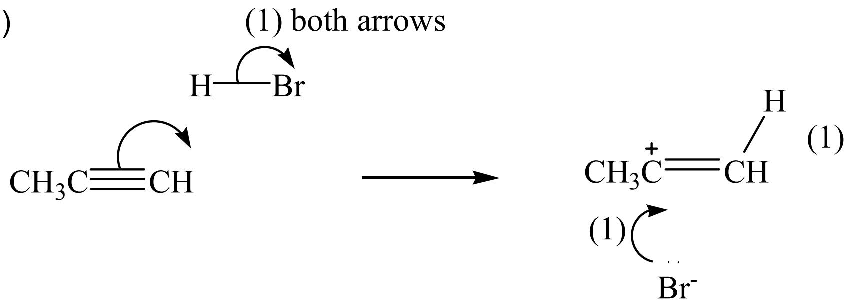
HCl + irritant / acidic fumes + use fume cupboard etc (1) **4**
(*Not just hazardous / harmful fumes*)

	(ii)	Single peak in spectrum	(1)	
		Octagonal molecule with alternating P and N atoms and 2 Cl atoms on each P	(1)	
		With alternating double and single bonds	(1)	
		Tetrahedral around each P	(1)	
		OR		
		4 N atoms in a square	(1)	
		P on each N + 2 × Cl on each P	(1)	
		Pyramidal around each P (allow tetrahedral)	(1)	**4**
		(Any other structures CE)		
(e)	(i)	$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	(1)	
		$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$	(1)	
		$KClO_3 + 3SO_2 + 3H_2O \rightarrow KCl + 3H_2SO_4$		
		OR		
		$ClO_3^- + 3SO_2 + 3H_2O \rightarrow Cl^- + 6H^+ + 3SO_4^{2-}$	(1)	**3**
	(ii)	**D** Moles AgCl = $\frac{0.414}{143.4} = 2.89 \times 10^{-3}$ mol	(1)	
		$[ClO_3^-] = 0.0289$ mol dm^{-3} (*Allow 0.029 mol dm^{-3}*)	(1)	**2**
	(iii)	1 Moles Fe^{2+} in 30.00 cm^3 = 6.30×10^{-3}mol	(1)	
		2 Moles $Cr_2O_7^{2-}$ in 8.20 cm^3 = 1.85×10^{-4} mol	(1)	
		3 Excess moles Fe^{2+} = $1.85 \times 10^{-4} \times 6 = 1.11 \times 10^{-3}$ mol	(1)	
		4 Moles Fe^{2+}reacted with ClO_3^- = $6.30 \times 10^{-3} - 1.11 \times 10^{-3}$ = 5.19×10^{-3} mol	(1)	
		5 Ratio moles $Fe^{2+}:ClO_3^-$ = $5.19\times 10^{-3}: 8.66 \times 10^{-4}$ = 5.99:1 i.e. 6:1 6:1 ratio from data NOT from balanced equation / oxidation state changes (*Conseq. On [ClO^{3-}] from (ii)*)	(1)	
		6 $ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$ (*Allow correct equation if not contradicted by ratio from calculation*)	(1)	**6**

Total 30

Question 4

(a)	(i)	Empirical formula = CH	(1)	
		Molecular ion at *m/z* = 78 therefore M_r = 78	(1)	
		Molecular formula C_6H_6	(1)	
		All Hs equivalent since one signal in proton n.m.r	(1)	
		Q benzene	(1)	
		M_r =106 so CH_3CH_2 added	(1)	
		R ethylbenzene	(1)	
		(Concentrated HNO_3/H_2SO_4) is nitrating mixture/nitration	(1)	
		M_r =151 so mono-nitration	(1)	
		S, T and **U** 2-, 3- and 4-ethylnitrobenzene	(1)	**10**
	(ii)	Repeating units for **V** and **W**: *cis-* and *trans*-poly(ethynes) (*Ignore brackets and 'n'*)	2 × (1)	
		Cis-trans isomerism/geometrical isomerism	(1)	**3**
(b)	(i)			

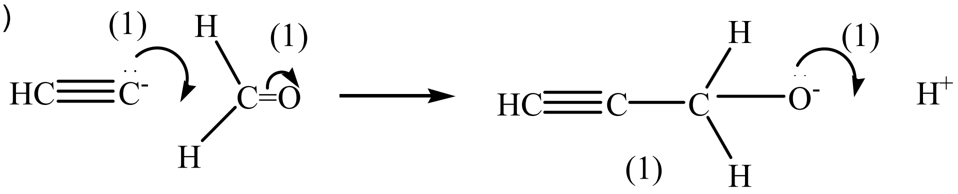


3

(Lone pairs needs not be shown)

	(ii)	3-D tetrahedral structure around chiral C of $CH_3CHBrCH_2Br$	(1)	
		Mirror image	(1)	
		Y $CH_3CBr_2CH_3$	(1)	**3**

(c) (i)



4

(Lone pairs needs not be shown)

(ii) Conversion 1: $NaNH_2$ (1)

$CH_3CH_2CH_2Cl$ / $CH_3CH_2CH_2Br$ / $CH_3CH_2CH_2I$ (1)

Conversion 2: $NaNH_2$ (1)

CH_3CHO (1)

Conversion 3: H_2/Ni (1)

Conversion 4: acidified potassium dichromate (1)

Z $CH_3CH(OH)CH_2CH_2CH_2CH_2CH_3$ (1) **7**

(Allow name or formulae for reagents)
(If 3 and 4 reversed or incorrect Z is not conseq.)

Total 30

Question 5

(a)	T1	Electronic configuration Ti +3: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ **and** electronic configuration Ti +4: $1s^2 2s^2 2p^6 3s^2 3p^6$ (*Not [Ar]3d^1 and [Ar])*	(1)	
	T2	3d electron well screened from nucleus by full s and p orbitals/ Inner electrons	(1)	
	T3	<u>Relatively</u> low energy requirement to lose this electron / <u>relatively</u> low ionisation energy	(1)	
	T4	More than compensated by energy released by new bonds formed in Ti(IV) compound	(1)	
	T5	Ti +3 compound coloured - Ti +4 compounds colourless / white	(1)	
	T6	Transition metal ion characteristics/colour associated with partially filled d subshell	(1)	
	T7	Ti +3 has I unpaired d electron, Ti +4 has no d electrons	(1)	**7**
	C1	Complex ion formation	(1)	
	C2	Vacant d orbitals	(1)	
	C3	Which can accept electron pairs from ligands	(1)	**3**
	S1	Electronic structure of Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ (*Allow [Ar] 3d^2 4s^2)*	(1)	
	S2	One 4s electron promoted to empty 3d orbital	(1)	
	S3	(Giving) four unpaired electrons so four covalent bonds can be formed	(1)	
	S4	The four bonding /electron pairs repel to distance of maximum Separation / minimum repulsion	(1)	
	S5	Tetrahedral molecule	(1)	
	S6	Hydrolysed by / reacts with the water vapour in moist air	(1)	
	S7	Forming hydrogen chloride fumes	(1)	
	S8	Balanced equation giving products as TiO_2 or $TiO_2.xH_2O$ or $T_1(OH)_4$ and HCl e.g. $TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$	(1)	**8**

	P1	Addition polymerisation	(1)	
	P2	Structural formulae of propene and repeat unit of poly(propene)	(1)	
	P3	Balanced equation	(1)	**3**
			17 max	
QWC	Correct use of technical language in at least two sections		(1)	
	Written in sentences and all four sections considered		(1)	
	Answers presented in logical form in not less than three sections		(1)	**3**
			Total 20	

Question 5

(b) M1 to M6 METHOD MARKS

Titration Method

M1	Mix known concentration of sodium hydroxide	(1)
M2	With an excess of 2-bromopropane (in ethanol)	(1)
M3	After measured time interval	(1)
M4	Remove sample with pipette	(1)
M5	Add to (cold) water to stop/quench reaction	(1)
M6	Titrate with standard acid	(1)

OR

pH / spectroscopy method

M1	Mix known concentration of sodium hydroxide	(1)
M2	With an excess of 2-bromopropane in ethanol	(1)
M3	Start time on mixing	(1)
M4	Use pH probe or spectrophotometer	(1)
M5	Measure pH or absorption <u>at fixed frequency</u>	(1)
M6	At regular intervals	(1)

OR

$AgNO_3$ METHOD

M1 and M2 only (2)

M7 TO M11 PROCESS MARKS

M7	Repeat sampling at specified time intervals *OR* Repeat experiment varying the initial concentration of NaOH	(1)
M8	Titre or measured quantity varies with to $[OH^-]$ / calculate different $[OH^-]$	(1)
M9	Plot graph of $[OH^-]$ v time / multiple repeats and calculations (minimum 5)	(1)

	M10	Calculate rate from gradients of graph *OR* from graph calculate the time for $[OH^-]$ to half at least twice *OR* compares at least four calculated values	(1)	
	M11	Plot graph of rate v $[OH^-]$ - straight line if first order wrt $[OH^-]$ *OR* times to half the $[OH^-]$ are constant *OR* draw conclusions from calculated values	(1)	**11**
	O1	2-bromobutane is chiral/has 4 different groups attached to a carbon atom	(1)	
	O2	Rotation of plane of plane polarised light/ using a polarimeter	(1)	
	O3	Planar intermediate can be attacked from either side	(1)	
	O4	Equal amounts of both isomers/a racemic mixture formed	(1)	**4**
	R1	Iodo- fastest; chloro- slowest	(1)	
	R2	Due to bond strength increasing in order C-I < C-Br < C-Cl	(1)	**2**
	B1	Benzene ring has a delocalised (Π) electron system	(1)	
	B2	Lone pair on Br atom enters into delocalised ring	(1)	
	B3	Strengthens the C-Br bond /decreases the polarity of the bond/ gives the C-Br bond double bond character	(1)	
	B4	Delocalised electrons repel negative hydroxide ion/ high activation energy requirement to overcome stabilisation energy of delocalised ring	(1)	**4**
			17 max	
QWC	Correct use of technical language in at least two sections;		(1)	
	Written in sentences and all four sections attempted;		(1)	
	Answers presented in a logical form in not less than three sections;		(1)	**3**
			Total 20	