MARKSCHEME

May 1999

CHEMISTRY

Higher Level

Paper 2

SECTION A

1. (a)
$$4C(s) + 4H_2(g) + O_2(g) \rightarrow C_3H_2COOH(l)$$

[1 mark]

Notes: Insist on correct state symbols

In (b), (c), and (d), omission of super and subscripts is not penalised.

(b)
$$\Delta H_{f(\text{rxn})}^{\circ} = \sum \Delta H_{f(\text{products})}^{\circ} - \sum \Delta H_{f(\text{reactants})}^{\circ}$$

[1 mark]

Note: Give [1 mark] if subsequent working is correct.

$$-21835 \text{ kJ} = \left[4(-3935 \text{ kJ mol}^{-1}) + 4(-285.9 \text{ kJ mol}^{-1})\right]$$
$$-\left[1(\Delta H_{f(\text{butanoic acid})}^{*}) + 5(0.0 \text{ kJ mol}^{-1})\right]$$

[1 mark]

Note: Give [1 mark] for correct substitution.

$$-2183.5 \text{ kJ} = [(-1574 \text{ kJ}) + (-1143.6 \text{ kJ})] - [1(\Delta H_f^*) + 0.0 \text{ kJ}]$$

$$-2183.5 \text{ kJ} = [(-2717.6 \text{ kJ})] - [1(\Delta H_f^{\circ})]$$

$$\Delta H_f^{\circ} = 2183.5 \text{ kJ} - 2717.6 \text{ kJ}$$

$$\Delta H_f^* = -534.1 \text{ kJ or kJ mol}^{-1}$$

[1 mark]

Note: Relate (b) to equation in (a) even if (a) is wrong max [3 marks].

(c)
$$\Delta S_{f(\text{butanoic acid})}^{\circ} = \Delta S_{(\text{butanoic acid})}^{\circ} - \left[4 S_{(\text{C})}^{\circ} + 4 S_{(\text{H}_{1})}^{\circ} + S_{(\text{O})}^{\circ} \right]$$

[1 mark]

[1 mark]

$$=-523.9 \text{ J mol}^{-1} \text{ K}^{-1} \text{ OR} - 0.5239 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

[1 mark]

Note: Relate (c) to equation in (a), even if (a) is wrong

(d)
$$\Delta G_f^{\circ} = \Delta H_f^{\circ} - T \Delta S_f^{\circ}$$
 (may be assumed if answer correct)

[1 mark]

$$= -534.1 \text{ kJ} - (298 \text{ K})(-0.5239 \text{ kJ K}^{-1})$$

$$= -378.0 \text{ kJ or kJ mol}^{-1}$$

[1 mark]

Note: Answers to (b), (c) and (d) must be consistent with (a)

(e) It is spontaneous since ΔG is negative

Need all for [1 mark]

[Consequently, if in (d) ΔG is given as positive, then reaction is **not** spontaneous]

Total [10 marks]

- 2. (a) (i) A solid (liquid not acceptable and high M_r not acceptable) [1 mark]
 Relatively large van der Waal's / intermolecular forces / H-bonding
 Note: Must have some discussion of bonding forces
 - (ii) The large number of C-C and C-H bonds / the long non-polar chain outweighs the polar OH. [1 mark]

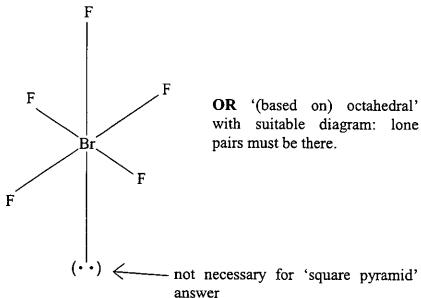
Allow [1 mark] for simply stating non-polar molecular

- (b) BF₃ has only three pairs of electrons about the central B atom.

 NF₃ has four pairs of electrons about the central N atom.

 [1 mark]

 or explanation in terms of sp²/sp³
- (c) Square pyramid [1 mark]



(d) one (sp) σ bond $\sigma/\pi=1$ [1 mark] and two π bonds [1 mark]

Triple bond for 1 compensatory mark

 $2\sigma, 1\pi = 1$ $1\sigma, 1\pi = 1$

if C_2H_4 , "double" = 0 1σ , $1\pi = 1$

Total [10 marks]

[1 mark]

Total [4 marks]

(a) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$ insist on [] 3. [1 mark] [NO₂] increases or yield increases (b) (i) [1 mark] since $[N_2O_4]$ increases and K_c is constant [1 mark] OR equilibrium moves to the right (ii) [NO₂] decreases or yield decreases [1 mark] since increased pressure pushes equilibrium to the left [1 mark] OR by Le Chatelier's Principle the smaller volume is favoured (iii) [NO₂] unchanged or yield unchanged [1 mark] catalyst does not affect position of equilibrium [1 mark] OR both forward and backward reaction rates affected equally $N_2O_4 \rightleftharpoons 2NO_2$ (c) (i) [1 mark] (ii) $\frac{(0.4)^2}{0.8} = 0.2 \text{ mol dm}^{-3}$ [2 marks] Note: Carry forward error from (a) in both numerical answer and units Error carried forward in (c) (ii), e.g. if [NO₂] is given as 0.2 then $K_{c} = 0.05$ (d) K_c increased [1 mark] [1 mark] since forward reaction is endothermic equilibrium moves to right as temperature increases Total [14 marks] 4. 2 (a) [1 mark] (b) 1 [1 mark] Rate = $k[A]^2[B]$ [] must be used (c) [1 mark] $0.5 = k(0.2)^2(0.2)$ k = 62.5(d) ептог carried forward from (c) [1 mark] Total [4 marks] 5. (a) Step 1 since it is the slowest. (Explanation must be given.) [1 mark] (b) Step 1 [1 mark] Slowest step, therefore has a higher activation energy relative to Step 2. [1 mark] Rate = $k[NO_2][F_2]$ (c) mark consequentially on (a) [1 mark]

SECTION B

6.	(a)	s, p, 1 em p, s,	For, for example s, p, f, d or p, s, d, f deduct l mark	[2 marks]
	(b)	<i>d</i> =	5, f = 7, p = 3, s = 1	4 correct [2 marks] 2 or 3 correct [1 marks]
		Any	answer which suggests the above	1 correct [0 marks]
	(c)	Any	2 from 3:	
	` ′		trons move (to lower) energy levels/orbitals	[1 mark]
			ting energy as they do so	[1 mark]
			tation and/or promotion to higher energy level	[1 mark]
	(d)		singly before doubling e two electrons in the same orbital will repel/Hund's rule/orbital	[1 mark]
			enerate	s are [1 mark]
		_	$s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ or reversed or Ar $3d^2 4s^2$	[1 mark]
			e: Must be superscript: 1s ²	į i markj
	(e)	(i)	Order must be correct:	
			Mass spectrometer.	[1 mark]
			A sample of naturally occurring gallium vapour	[1 mark]
			is injected into the evacuated ionising chamber where an elec beam ionises a part of the sample by knocking electrons from	tron
			neutral atoms or molecules.	[1 mark]
			Charged plates accelerate the positive ions towards the dete and the ions pass through a magnetic field perpendicular to	ector [1 mark]
			path	(1 mark)
			where the charged ions are separated (deflected) into diffe	
			paths.	[1 mark]
			The detector detects the paths according to the masses of	
			particles.	[1 mark]
			Accept labelled diagram and adequate explanation.	
			Any five points from the six given.	[max 6 marks]
		(ii)	Ga-69 31p 38n	[I mark]
		` '	Ga-71 31p 40n	[1 mark]
			$(60 \times 69) + (40 \times 71)$	[1 mark]
			100	į i murkj
			69.8	[1 mark]

Question 6 continued...

(f) (i) removed from a positively charged ion, Be⁺(g), whereas [1 mark] the first electron is removed from a neutral atom, Be(g). [1 mark]

1st electron is removed from a full sub-orbital; 2nd electron is removed from a singly occupied sub-orbital, gains [1 mark] only

(ii) Electron from 3p in Al but electron from 3s in Mg which is of lower energy

[1 mark] [1 mark]

(iii) Electron from 2(p) in B ('p' not essential) Electron from 3(p) in Al ('p' not essential)

[1 mark]

The latter is further from the nucleus / the former is nearer to the nucleus

[1 mark]

Total [25 marks]

7. (a) (i) NaHCO₃: Brønsted-Lowry base because proton acceptor, [1 mark]
Lewis base because electron pair donor. [1 mark]
CaCO₃: Both [1 mark]

(ii) $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ [1 mark]

OR NaHCO₃ + HCl \rightarrow NaCl + H₂O + CO₂

Note: If H₂CO₃, no mark given.

 $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$ [2 marks]

OR $Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$

OR $Al(OH)_3(H_2O)_3 + 3H^+ \rightarrow [Al(H_2O)_6]^{3+}$

Note: [1 mark] for correct species, [1 mark] for correct balance.

 $CaCO₃ + 2H⁺ \rightarrow Ca²⁺ + H₂O + CO₂$ $+2HCl \rightarrow CaCl₂$ [1 mark]

Note: If H₂CO₃ again, do not penalise.

(iii) $n_{\text{mol}} \text{NaHCO}_3 = 1 \text{ g} \times \frac{1 \text{ mol}}{84 \text{ g mol}^{-1}} = 0.012$ [1 mark]

 $n_{\text{mol}} \text{Al(OH)}_3 = 1 \text{ g} \times \frac{1 \text{ mol}}{78 \text{ g mol}^{-1}} = 0.013$ [1 mark]

 $n_{\text{mol}} \text{CaCO}_3 = 1 \text{ g} \times \frac{1 \text{ mol}}{100 \text{ g mol}^{-1}} = 0.010$ [1 mark]

Al(OH)₃ reacts with 3 mol of H⁺ so it is more effective than CaCO₃ which reacts with 2 mol of H⁺ which is more effective than NaHCO₃ which reacts with 1 mol of H⁺

[3 marks]

OR Al(OH)₃ best [1 mark]
CaCO₃ a further [2 marks] if stoichiometry [1 mark]
NaHCO₃ worst has been used to explain the rest of the order

Note: If order is wrong look for consequential marking

(iv) NaOH is a strong alkali
damages body tissues / corrosive to body
difficult to store

[1 mark]

Note: Accept other answers on merit

Question 7 continued...

(b) (i) amphoteric/amphiprotic [1 mark]

(ii) $Zn(OH)_2 + 2H^+ \rightarrow Zn^{2+} + 2H_2O$ equation 1, balanced 1 [2 marks] $Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-}$ (OR $ZnO_2^{2-} + 2H_2O$) [2 marks]

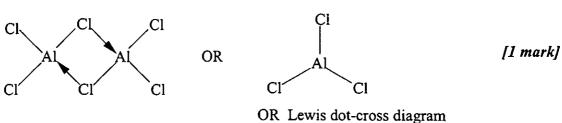
 $Al(OH)_3 / Pb(OH)_2 / Sn(OH)_2 / Al_2O_3 / Cr(OH)_3$ / accept other [1 mark] suitable oxides/hydroxides (not H₂O)

(iii) Electron pair acceptor. [1 mark]
They have available / empty (d) orbitals. [1 mark]

e.g. $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$ [2 marks] choice of base (ligand) 1, formula of suitable complex 1 Total [25 marks]

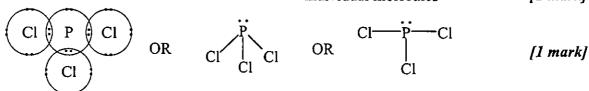
N.B. $[Cu(H_2O)_4]^{2+}$ or $[Cu(H_2O)_6]^{2+}$, both are acceptable Note: Equation does not have to be balanced

- 8. (a) (i) NaCl high melting and boiling points giant structure/ionic [1 mark] strong attraction between ions [1 mark]
 - $Na^{+} \begin{bmatrix} \vdots C \vdots \end{bmatrix}^{-} OR$ $Na^{+} \begin{bmatrix} \vdots C \vdots \end{bmatrix}^{-} OR$ $Cl^{-} \begin{bmatrix} Na^{+} & Cl^{-} & Na^{+} \\ & & & \\ & &$
 - Al₂Cl₆ low melting and boiling points simple molecular/covalent associated or weak forces between individual molecules [1 mark]



PCl₃ - low melting and boiling points - simple molecular/covalent [1 mark]

weak forces between individual molecules [1 mark]



- (ii) NaCl dissolves (do not accept dissociates) [1 mark]
 AlCl₃ vigorous reaction /exothermic/fizzing/gas evolved [1 mark]
 PCl₃ gives vigorous reaction/exothermic/fizzing/gas evolved [1 mark]
 AlCl₃ + 3H₂O \rightarrow Al(OH)₃ + 3HCl [1 mark]
 PCl₃ + 3H₂O \rightarrow H₃PO₃ + 3HCl [1 mark]
- (b) (i) ionic, ionic, covalent, covalent [4 marks]
 - (ii) strong alkali, weak alkali, nothing, acid
 OR OR OR OR
 high pH pH above 7 7 below 7

 $Na_2O + H_2O \rightarrow 2NaOH$ Give [1 mark] [1 mark] $MgO + H_2O \rightarrow Mg(OH)_2$ if product [1 mark] $P_4O_6(P_2O_3) + 6H_2O(3H_2O) \rightarrow 4H_3PO_3(2H_3PO_3)$ is correct [1 mark] OR $P_4O_{10}(P_2O_3) + 6H_2O(3H_2O) \rightarrow 4H_3PO_4(2H_3PO_4)$ 9. (a) (i) $C_4H_{10}O = 74$ Therefore molecular formula = $C_4H_{10}O$

[1 mark]
[1 mark]

(ii) Removal of $CH_3 / C_3H_7O^+$ is present

[1 mark]

(iii) OH

[1 mark]

(b) CH₃CH₂CH₂CH₂OH

[2 marks]

- (c) (i) C=C (or alkene) accept 'primary alcohol' or -CH₂OH if [1 mark] candidate has misinterpreted the question
 - (ii) $CH_3CH_2CH = CH_2$
- CH₃—C—CH₃
 ||
 CH₂

[2 marks]

(iii) CH₃CH₂CH(Cl)CH₃ CH₃CH₂CH₂CH₂Cl

[3 marks]

(d) CH₃—C—CH || CH₂

[1 mark]

The phrasing of the question may lead candidates to offer more than one answer. Give credit for correct answer – ignore the rest.

Question 9 continued...

- (e) (i) substitution [1 mark]
 nucleophilic [1 mark]
 1st order/unimolecular [1 mark]
 - (ii) Steric effects of CH₃ [1 mark]
 CH₃ electron releasing
 The (CH₃)₃C⁺ ion is stable

 [1 mark]
 [1 mark]

(iii)
$$CH_3 - C_{\delta} CI \xrightarrow{SLOW [1 \text{ mark}]} CH_3 - C_{H_3} \xrightarrow{CH_3} CH_3 - C_{H_3} CH_3 - C_{H_3} CH_3$$

polarity [1 mark] OH ion + product [1 mark] [5 marks]

Note: If candidate has given a lot of detail in (e)(i), carry forward credit to (e)(iii).

(f) A tertiary alcohol cannot be oxidised.

[I mark]

Total [25 marks]