# **MARKSCHEME**

November 2000

**CHEMISTRY** 

**Higher Level** 

Paper 2

#### **SECTION A**

**1.** (a) (i) A, C, D

(Must have all three for mark.)

(ii) A [1]

- (iii) van der Waal's forces (or dispersion or London forces or induced dipole induced dipole (but **not** dipole–dipole) interaction). [1]
- (iv) Nitrogen or oxygen or fluorine. [1]
- (v) F because it has the highest melting/boiling point. [1]

(Need explanation for mark.)

(vi) E: a metal; [1]
F: a metalloid (accept semi-conductor). [1]

(b) (i) 
$$\delta - \delta + O - H - O$$
 CH<sub>3</sub> C—CH<sub>3</sub> [1]

Exists as a dimer in non-polar solvents (because of strong inter-molecular H-bonding) but exists as a monomer in aqueous solution (because of H-bonding with water). [1]

(No mark without mention of non-polar solvent.)

(ii) 
$$H$$
  $C = C$   $O =$ 

(Award [1] for diagram showing intra-molecular H-bonding)

The cis-isomer experiences **intra**-molecular H-bonding that reduces the chances of H-bonding between molecules;

**OR** the trans-isomer experiences (more) **inter**-molecular H-bonding that increases the chances of H-bonding between molecules.

## Question 1 (b) continued

(iii) 
$$\delta_{+}$$
 H  $C_{2}H_{5}$   $C_{2}H_{5}$   $C_{2}H_{5}$  [1]

Only ethanol experiences H-bonding because H is bonded to O, whereas in the ether, all H atoms are bonded to  ${\bf C}$ 

**OR** ether does not exhibit H-bonding as H is not bonded to O. [1]

**2.** (a) (i)

(ii) +2

	4s			3d		
Fe <sup>0</sup> :	$\uparrow \downarrow$	$\uparrow \downarrow$	<b>↑</b>	<b>↑</b>	<b>↑</b>	<b>↑</b>
Fe <sup>2+</sup> :		$\uparrow \downarrow$	<b>↑</b>	<b>↑</b>	<b>↑</b>	<b>↑</b>
Fe <sup>3+</sup> :		<b>↑</b>	<b>↑</b>	<b>↑</b>	<b>↑</b>	$\uparrow$

(Award [1] for each correct electronic configuration.)

[3]

[1]

(iii)  $\operatorname{FeO}_4^{2-}$ , **OR**  $\operatorname{FeO}_3$  **OR**  $\operatorname{Fe}_2\operatorname{O}_7^{2-}$  **OR**  $\operatorname{Fe}_2\operatorname{O}_6$ 

[1]

(b) (i) A ligand is an anion or a molecule (having lone electron pairs) that can form a (co-ordinate) bond to a (central) atom or cation.

[1]

(ii) A Lewis acid-base reaction

[1]

The ligand is a Lewis base (or an electron pair donor) **and** the metal ion a Lewis acid (or an electron pair acceptor).

[1]

**OR** because H<sub>2</sub>O donates an e<sup>-</sup> pair to form a covalent bond with Fe<sup>2+</sup>

(Need both comments for mark.)

(iii) Because the d orbitals are split into two sets of different energy levels **and** electron transitions between them are responsible for their colours.

[1]

(Need both statements for mark.)

Different ligands split to different extent giving different colours.

[1]

**OR** They contain different ligands, so the energy difference between the split 3d orbitals is not the same in each case.

The e transitions between the two absorb different amounts of energy, corresponding to different wavelength of light in the visible spectrum.

3. (a) (i) 
$$t^{\frac{1}{2}} = \frac{0.693}{k}$$
;  $k = \frac{0.693}{162 \times 10^4 \text{ s}}$ 

$$=4.28\times10^{-5} \text{ s}^{-1}$$

(No mark without units.)

(ii) 
$$\ln k = \frac{-E_a}{RT} + \ln A$$

Therefore  $E_a = (\ln A - \ln k) RT$ 

=
$$[3.219 - (-10.059)] \times 8.314 \text{ J K}^{-1} \times 1107 \text{ K}$$
 [1]

(Award [1] for correct temperature.)

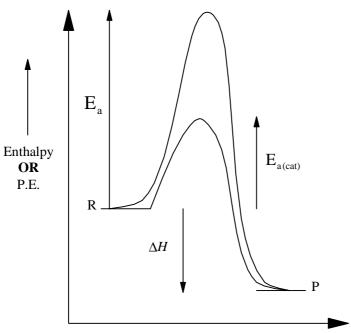
$$= 122 \text{ kJ}$$
 [1]

(No mark without unit. If T taken as 834  $^{\circ}$ C, then  $E_a = 92.1 \text{ kJ}$ )

(iii) Slow step: 
$$N_2O + N_2O \rightarrow N_4O_2$$
 **OR**  $N_2O + N_2O \rightarrow N_2O_2 + N_2$  [1]

Fast step: 
$$N_4O_2 \to 2N_2 + O_2$$
 **OR**  $N_2O_2 \to N_2 + O_2$  [1]

(b)



(reaction coordinate or progress of reaction or  $t \longrightarrow$ )

(Award [1] for exothermic reaction and [1] for  $E_a$  and  $E_{a(cat)}$ . Allow [1] for showing  $E_a$  lower for catalysed reaction.)

[2]

4. There will be no change in pressure. (a) (i)

[1]

The pressure will decrease. (ii)

[1]

[1]

The temperature will increase. (b) (i)

(ii) The methanol concentration will increase. [1]

(c) (i) 
$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} \text{ mol}^{-2} \text{ dm}^6$$

[1]

[1]

[1]

(Need units to score mark.)

(ii) 
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$
  $\Delta H = -91 \text{ kJ mol}^{-1}$ 

$$\Delta H = -91 \text{ kJ mol}^{-1}$$

n:

1.00

2.00

neq:

1.00 - 0.85

2.00 - 1.70

0.85

[]eq:

0.15 0.45 0.30 0.45 0.85 0.45

= 0.333

= 0.667

Side reactions **OR** leaks in the system **OR** not operating under equilibrium conditions OR operating at a higher temperature OR the product might be

= 1.889

$$K_{\rm c} = \frac{1.889}{0.333 \times 0.667^2}$$

$$= 12.8 \, (\text{mol}^{-2} \, \text{dm}^6)$$

[1]

[1]

(iv) No effect on  $K_c$  (it just speeds up the reaction).

collected before equilibrium is reached.

## **SECTION B**

5.	(a)	(i)	Electrons go into <b>same</b> main shell/energy level. <b>Increase</b> in nuclear charge <b>OR</b> number of protons in the nucleus across period (pulls valence electrons closer together).	[1] [1]		
		(ii)	Mg is 3s <sup>2</sup> , Al is 3s <sup>2</sup> 3p <sup>1</sup> .  The 3p <sup>1</sup> electron is in a higher energy level and easier to remove.	[1] [1]		
		(iii)	P is 3p <sup>3</sup> where the electrons are arranged singly; S is 3p <sup>4</sup> Repulsion of the paired electron in S causes lower I.E.	[1] [1]		
	(b)	NaCl, MgCl <sub>2</sub> , AlCl <sub>3</sub> (Al <sub>2</sub> Cl <sub>6</sub> ), SiCl <sub>4</sub> , PCl <sub>5</sub> or PCl <sub>3</sub> .				
		(Award [2] for all correct and [1] for one error.)				
		Argo	on is a noble (unreactive) gas with full outer shell of electrons.	[1]		
			4: covalent bonding between atoms (within the molecules). ak van der Waal's or London or dispersion forces between molecules.	[1] [1]		
	(c)	oxid	des of Na and Mg: basic; le of Al: amphoteric; le of Si, P and S: acidic.	[1] [1] [1]		
		(Awa	ard no marks for any one missing; formulas of oxides not asked for.)			
		_	$O + H_2O \rightarrow Mg(OH)_2$ $_{10} + 6H_2O \rightarrow 4H_3PO_4 \text{ (accept } P_2O_5 + 3H_2O \rightarrow 2H_3PO_4)$	[1] [1]		
		(Accept appropriate acid-base reactions; equations must be balanced to score marks.)				
		_	htly acidic from dissolved $CO_2$ in water forming carbonic acid <b>OR</b> $_2 + H_2O \rightarrow H_2CO_3$ (weak acid) ( <i>No mark if SO<sub>x</sub> or NO<sub>x</sub> mentioned</i> )	[1]		
	(d)	(i) OR	$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ (accept $2Na^+AlO_2^- + H_2O$ ) $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$ (accept $2Na^+Al(OH)_4^-$ )	[1] [1]		
			(Accept net ionic equations; equations must be balanced for marks.)			
		(ii) OR	$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{3+} + H^+$ $FeCl_3 + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+} + 3Cl^-$	[1]		
	(e)	as it $Br_2$ as it	reacts with (oxidises) $Br^-$ and $I^-$ to the corresponding halogens is a better oxidising agent than $Br_2$ and $I_2$ . (Accept balanced equations) reacts with $I^-$ but not $Cl^-$ (to form $I_2$ ) (accept balanced equation) is a better oxidising agent than $I_2$ .	[1] [1] [1] [1]		

 $\Delta H_f^{\circ}$  = standard enthalpy change of formation of a substance. 6. (a) [1] It is the heat **change** (absorbed or released under constant pressure) when a mole of a compound is formed from its elements in their standard states. [1]  $S^{\circ}$  = standard entropy. [1] It is related to (is a measure of) the disorder or randomness of particles. [1] **OR** It is the quantity of energy owned by a mole of an element or a compound in its standard state at 298 K. A: related to standard conditions or 298 K (25  $^{\circ}$ C) and one atmosphere pressure. (Need both for mark.) [1]  $\Delta$ : not included because S has absolute values, **OR** S values can be measured. [1] (ii) (iii)  $\Delta H_f^{\circ}(Cu) = 0$ [1] (i)  $\Delta H_f^{\circ}$  reaction =  $\sum \Delta H_f^{\circ}$  products -  $\sum \Delta H_f^{\circ}$  reactants (b) [1] (Can be implicit in the calculation)  $\Delta H_f^{\circ}$  reaction =  $\{[4 \times (-242) + (-1084)] - [-2278]\}$  kJ mol<sup>-1</sup> [1]  $= +226 \text{ kJ mol}^{-1} (accept kJ)$ [1] (Must include unit to score mark.) [1] An endothermic process **OR** reaction needs energy/heat (ii)  $\Delta S^{\circ}$  reaction =  $\sum \Delta S^{\circ}$  products -  $\sum \Delta S^{\circ}$  reactants =  $\left[ \left[ \left[ 4 \times (189) + (150) \right] - \left[ 305 \right] \right] \int K^{-1}$ [1]  $\Delta S^{\circ}$  reaction = 601 J K<sup>-1</sup> **OR** 0.601 kJ K<sup>-1</sup> (correct value) [1] (correct units) [1] [1] (+) sign/value, thus products are more disordered than reactants. (iii) Gibbs free energy, **OR** G (accept  $\Delta G$ ). [1]

Units: J or kJ **OR** kJ mol<sup>-1</sup>.

#### Question 6 continued

(c) (i) 
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
  
= 226 kJ - 298 K (0.601 kJ K<sup>-1</sup>)

(Award [1] for temperature and [1] for 
$$\Delta H^{\circ}$$
 and  $\Delta S^{\circ}$  values.) [2]

= 
$$+47 \text{ kJ (accept } 47 \text{ kJ mol}^{-1}; \text{ no marks without units)}$$
 [1]

$$\Delta G^{\circ} > 0$$
, therefore reverse action is spontaneous. [1]

**OR** forward reaction is non-spontaneous

thus 
$$CuSO_4 \cdot 5H_2O$$
 is more stable at 25 °C. [1]

(No double jeopardy if wrong answers are used from (b) above.)

(ii) 
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

Therefore 
$$0 = 226 \text{ kJ} - TK (0.601 \text{ kJ K}^{-1})$$
 [1]

Therefore 
$$T = \frac{226}{0.601} = 376 \text{ K}$$
. [1]

Thus forward reaction is spontaneous above 
$$103 \,^{\circ}\text{C}$$
 [1] (i.e.  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  is more stable above  $103 \,^{\circ}\text{C}$ ).

<b>7.</b> (a)	(a)	(i)	Weak acid for a strong 0.100 mol dm <sup>-3</sup> , pH would be 1.0	
			(thus acid is partially dissociated and weak).	[1]
			pH of final solution closer to 13 means $pOH = 1$ <b>OR</b> there is a substantial	[1]
			vertical portion of the pH curve near the end point	[1]
			thus a strong base.	
			25.0	
		(ii)	$V_b = 0.100 \text{ mol dm}^{-3} \times \frac{25.0}{22.2}$ .	[1]
			22.2	[1]
			$= 0.113 \text{ mol dm}^{-3}$ (accept M as unit).	[1]
			of 13 morani (weeept in an antic).	. ,
		(iii)	$HIn \rightleftharpoons H^+ + In^-$ (generally weak acids)	[1]
		` /		
			In acid solution, [H <sup>+</sup> ] will shift equilibrium to the left, indicator is	
			predominantly present as HIn which is one colour	[1]
			and in basic solution, H <sup>+</sup> ions are removed by OH <sup>-</sup> , shifting equilibrium to the	
			right; In predominantly present which is another colour.	[1]
			[H <sup>+</sup> ][In <sup>-</sup> ]	
		(iv)	$K_{\mathbf{a}} = \frac{[\mathbf{H}^+][\mathbf{In}^-]}{[\mathbf{HIn}]}$	[1]
			[HIII]	
			At end point intensity of HIn and In is about the same (where colour change	
			takes place), $\mathbf{OR}$ [HIn] = [In <sup>-</sup> ]	[1]
			therefore $K_a = [H^+]$ , and $pK_a = pH$ .	[1]
			more ra [11 ], and pra pri	L*J
		(v)	At equivalence point pH $\approx 8$ / between 8 and 9, so use indicator of p $K_a \approx 8$ .	

(Accept 9.)

#### Question 7 continued

(b) Na<sup>+</sup> ions are neutral cations from a strong base.

ethanoate ions are basic (from a weak acid)

OR CH<sub>3</sub>COO<sup>-</sup> + H<sub>2</sub>O ≠ CH<sub>3</sub>COOH + OH<sup>-</sup> OR hydrolyses to produce weak acid +

strong base, therefore basic.

Since ammonium ion is a weak acid OR NH<sub>4</sub><sup>+</sup> ≠ NH<sub>3</sub> + H<sup>+</sup>

[1]

then the presence of a weak acid and a weak base produces (an approximately) neutral solution.

Alternate answer:

The ions in sodium ethanoate solution are

- CH<sub>3</sub>COO<sup>-</sup> and Na<sup>+</sup>,
- H<sup>+</sup> and OH<sup>-</sup>.

 $Na^+$  and  $OH^-$  do not combine because NaOH is a strong base.  $CH_3COO^-$  and  $H^+$  do combine because  $CH_3COOH$  is a weak acid. The solution contains more  $OH^-$  than  $H^+$  ions, so is alkaline. The ions in ammonium ethanoate solution are

- CH<sub>3</sub>COO<sup>-</sup> and NH<sub>4</sub><sup>+</sup>,
- H<sup>+</sup> and OH<sup>-</sup>.

 $NH_4OH$  is a weak base, so the  $NH_4^+$  and  $OH^-$  ions combine. As this happens to about the same extent as the combination of  $CH_3COO^-$  and  $H^+$ , the numbers of  $H^+$  and  $OH^-$  ions are about equal, so the solution is approximately neutral.

- (c)  $SO_4^{2^-}$ : neutral anions (from a strong acid). [1]  $AI^{3+}$ : weakly acidic **OR**  $AI(H_2O)_6^{3+} \rightleftharpoons [AI(H_2O)_5(OH)]^{2^+} + H^+$ The  $H^+$  reacts with the basic solution, reducing its pH  $OR[AI(H_2O)_6]^{3^+} + OH^- \rightarrow [AI(H_2O)_5(OH)]^{2^+} + H_2O$
- (d) (i)  $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$  [1]

(accept  $NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + H_2O$ )

(ii) 
$$n = cV = 0.4040 \text{ mol dm}^{-3} \times 0.02851 \text{ dm}^{3} = 0.01152 \text{ mol}$$
 [1]

mol NH<sub>3</sub> = 2 mol acid = 
$$0.02304$$
 mol [1]  
 $M_r = 17.04$ ; mass =  $17.04$  g mol<sup>-1</sup> ×  $0.02304 = 0.3926$  g [1]  
(if  $M_r = 17.0$ , accept  $0.392$  g).

$$\% = \frac{0.3919}{2.447} \times 100 = 16.04 \%$$
 [1]

(Accept answers within + or - one s.f.; maximum penalty of [1] in question for serious errors in use of significant figures.)

8. C = C: add bromine (or bromine water) [1] its colour is discharged **OR** changes from orange to clear. [1] COOH: add sodium carbonate solution **OR** Na **OR** acid/base indicator. [1] It would effervesce/gas bubbles produced. [1] at 1610-1680 cm<sup>-1</sup> (b) (i) C = Cat 1680-1750 cm<sup>-1</sup> C = O[2] С—Н at 2840-3095 cm<sup>-1</sup> at 2500-3300 cm<sup>-1</sup> О—Н (Award [2] for three correct and [1] for any two.) (ii) CH<sub>3</sub> at 0.9 ppm C = C - H at 4.9–5.9 ppm COOH at 11.5 ppm [2] (Award [2] for all three and [1] for any two.) Ratio of areas of peaks: 6:1:1 [1] (c) (i) **NMR** [1] because B would give 5 peaks [1] whereas C would give only 4 peaks [1] (Accept: because the chemical environments of the H atoms are different and the number of peaks would be different.) Test based on fact that secondary alkanols (alcohols) area easily oxidised, whereas tertiary alkanols are not [1] Warm (or reflux) with acidified dichromate or manganate(VII) [1] With B orange dichromate would change to green (OR purple manganate(VII) would turn (almost) clear) [1] With C it would remain orange (or purple) [1] Optical activity is the ability to rotate the plane of polarised light (accept rotate (d) (i) plane polarised light). [1] It has an asymmetric carbon atom **OR** a carbon bonded to four different groups **OR** the molecule is asymmetric **OR** chiral centre. [1] (ii) Compound B can exhibit optical activity. [1]  $CH(CH_3)_2$  (accept  $C_3H_7$ )

CH(CH<sub>3</sub>)<sub>2</sub> CH(CH<sub>3</sub>)<sub>2</sub> (accept C<sub>3</sub>H<sub>7</sub>)

$$\downarrow$$
HOOC OH HO COOH

(Award only [1] if relationship is not clear.)

One enantiomer rotates plane of polarised light clockwise (or +), the other anticlockwise (or -); accept dexrorotatory and levorotatory.

[1]

### Question 8 continued

(e) For OH to be acidic, the O—H bond has to break/ $H^+$  or protons form

$$(--C-O-H-C-O-H+H+)$$

In COOH the O—H bond breaks/ $H^+$  forms because the second O on carbon attracts  $e^-$  density from the O—H bond.

Delocalisation stabilises the COO<sup>-</sup> anion. [1]