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BACCALAUREATE
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MARKSCHEME

November 2000

CHEMISTRY

Higher Level

Paper 2

17 pages

SECTION A

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

(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)

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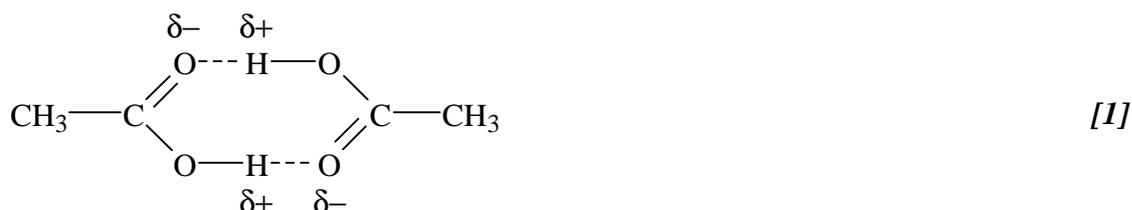
Exists as a dimer in non-polar solvents (because of strong inter-molecular H-bonding) but exists as a monomer in aqueous solution (because of H-bonding with water).   *[1]*

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

(ii)

[1]

(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;   *[1]*
OR   the trans-isomer experiences (more) **inter**-molecular H-bonding that increases the chances of H-bonding between molecules.

Question 1 (b) continued

(iii)

$$C_2H_5 \overset{\delta-}{O} \underset{H}{\overset{\overset{\delta+}{H} - O}{\diagdown}} C_2H_5$$
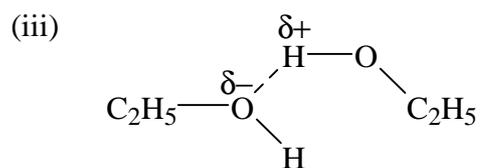
[1]

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

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

2.   (a)   (i)

	4s	3d				
Fe^0:	↑↓	↑↓	↑	↑	↑	↑
Fe^{2+}:		↑↓	↑	↑	↑	↑
Fe^{3+}:		↑	↑	↑	↑	↑

(Award [1] for each correct electronic configuration.)   *[3]*

     (ii)   +2   *[1]*

     (iii) FeO_4^{2-}, **OR** FeO_3 **OR** $Fe_2O_7^{2-}$ **OR** Fe_2O_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_2O donates an e^- pair to form a covalent bond with Fe^{2+}

(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) $t\frac{1}{2} = \dfrac{0.693}{k}$;

$$k = \dfrac{0.693}{1.62 \times 10^4 \text{ s}}$$

$$= 4.28 \times 10^{-5} \text{ s}^{-1} \qquad \qquad \textbf{[1]}$$

(No mark without units.)

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

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

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

(Award [1] for correct temperature.)

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

(No mark without unit. If T taken as 834 °C, then $E_a = 92.1$ 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: $N_4O_2 \rightarrow 2N_2 + O_2$ **OR** $N_2O_2 \rightarrow N_2 + O_2$ **[1]**

(b)

(reaction coordinate or progress of reaction or $t \rightarrow$)
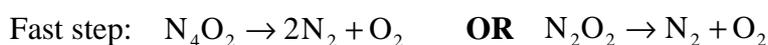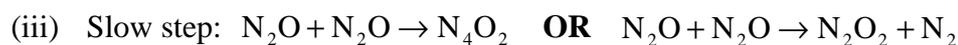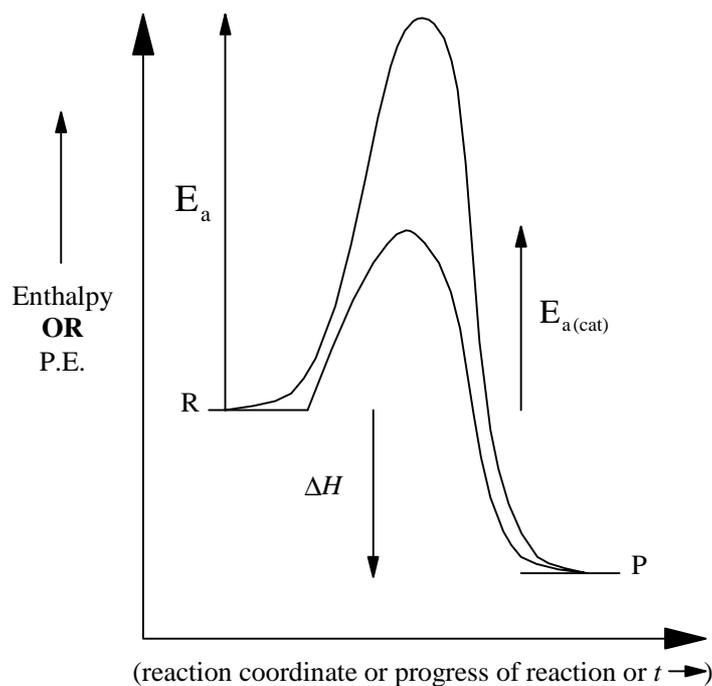
(Award [1] for exothermic reaction and [1] for E_a and $E_{a(cat)}$. Allow [1] for showing E_a lower for catalysed reaction.)   **[2]**

4. (a) (i) There will be no change in pressure. *[1]*

     (ii) The pressure will decrease. *[1]*

  (b) (i) The temperature will increase. *[1]*

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

  (c) (i) $K_c = \dfrac{[CH_3OH]}{[CO][H_2]^2}$ mol^{-2} dm^6 *[1]*

      (Need units to score mark.)

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

n:	1.00	2.00	–	
neq:	$1.00 - 0.85$	$2.00 - 1.70$	0.85	*[1]*
[]eq:	$\dfrac{0.15}{0.45}$	$\dfrac{0.30}{0.45}$	$\dfrac{0.85}{0.45}$	*[1]*
	$= 0.333$	$= 0.667$	$= 1.889$	
K_c	$= \dfrac{1.889}{0.333 \times 0.667^2}$		$= 12.8\,(\text{mol}^{-2}\,\text{dm}^6)$	*[1]*

     (iii) Side reactions **OR** leaks in the system **OR** not operating under equilibrium conditions **OR** operating at a **higher** temperature **OR** the product might be collected before equilibrium is reached. *[1]*

     (iv) No effect on K_c (it just speeds up the reaction). *[1]*

SECTION B

5. (a) (i) Electrons go into **same** main shell/energy level. *[1]*
Increase in nuclear charge **OR** number of protons in the nucleus across period
(pulls valence electrons closer together). *[1]*

(ii) Mg is $3s^2$, Al is $3s^2 3p^1$. *[1]*
The $3p^1$ electron is in a higher energy level and easier to remove. *[1]*

(iii) P is $3p^3$ where the electrons are arranged singly; S is $3p^4$ *[1]*
Repulsion of the paired electron in S causes lower I.E. *[1]*

(b) NaCl, $MgCl_2$, $AlCl_3$ (Al_2Cl_6), $SiCl_4$, PCl_5 or PCl_3. *[2]*

(Award [2] for all correct and [1] for one error.)

Argon is a noble (unreactive) gas with full outer shell of electrons. *[1]*

$SiCl_4$: covalent bonding between atoms (within the molecules). *[1]*
Weak van der Waal's or London or dispersion forces between molecules. *[1]*

(c) Oxides of Na and Mg: basic; *[1]*
oxide of Al: amphoteric; *[1]*
oxide of Si, P and S: acidic. *[1]*

(Award no marks for any one missing; formulas of oxides not asked for.)

$MgO + H_2O \rightarrow Mg(OH)_2$ *[1]*
$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ (accept $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$) *[1]*

(Accept appropriate acid–base reactions; equations must be balanced to score marks.)

Slightly acidic from dissolved CO_2 in water forming carbonic acid **OR**
$CO_2 + H_2O \rightarrow H_2CO_3$ (weak acid) *(No mark if SO_x or NO_x mentioned)* *[1]*

(d) (i) $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ *[1]*
$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ (accept $2Na^+AlO_2^- + H_2O$) *[1]*
OR $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$ (accept $2Na^+Al(OH)_4^-$)

(Accept net ionic equations; equations must be balanced for marks.)

(ii) $[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{3+} + H^+$ *[1]*
OR $FeCl_3 + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+} + 3Cl^-$

(e) Cl_2 reacts with (oxidises) Br^- and I^- to the corresponding halogens *[1]*
as it is a better oxidising agent than Br_2 and I_2. *(Accept balanced equations)* *[1]*
Br_2 reacts with I^- but not Cl^- (to form I_2) *(accept balanced equation)* *[1]*
as it is a better oxidising agent than I_2. *[1]*
I_2 will not react with Cl^- or Br^- (as it is the weakest oxidising agent of the three). *[1]*

6.   (a)   (i) $\Delta H_f^{\ominus}$ = standard enthalpy change of formation of a substance.   ***[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]***

$S^{\ominus}$ = 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.

À: related to standard conditions or 298 K (25 °C) **and** one atmosphere pressure. *(Need both for mark.)*   ***[1]***

   (ii)   À: not included because *S* has absolute values, **OR** *S* values can be measured.   ***[1]***

   (iii) $\Delta H_f^{\ominus}(\text{Cu}) = 0$ ***[1]***

   (b)   (i) $\Delta H_f^{\ominus}\,\text{reaction} = \sum \Delta H_f^{\ominus}\text{products} - \sum \Delta H_f^{\ominus}\text{reactants}$ ***[1]***

(Can be implicit in the calculation)

$\Delta H_f^{\ominus}\,\text{reaction} = \left\{\left[4\times(-242)+(-1084)\right]-\left[-2278\right]\right\}\text{kJ mol}^{-1}$ ***[1]***

$= +226\,\text{kJ mol}^{-1}$ *(accept kJ)*   ***[1]***

(Must include unit to score mark.)

An endothermic process **OR** reaction needs energy/heat   ***[1]***

   (ii) $\Delta S^{\ominus}\,\text{reaction} = \sum \Delta S^{\ominus}\text{products} - \sum \Delta S^{\ominus}\text{reactants}$
$= \left[\left[4\times(150)\right]-\left[305\right]\right]\text{J K}^{-1}$ ***[1]***

$\Delta S^{\ominus}\,\text{reaction} = 601\,\text{J K}^{-1}$ **OR** $0.601\,\text{kJ K}^{-1}$ (correct value)   ***[1]***
(correct units)   ***[1]***

(+) sign/value, thus products are more disordered than reactants.   ***[1]***

   (iii)   Gibbs free energy, **OR** *G* (accept ΔG).   ***[1]***
Units: J or kJ **OR** kJ mol^{-1}.   ***[1]***

continued...

Question 6 continued

(c) (i) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
$= 226 \text{ kJ} - 298 \text{ K } (0.601 \text{ kJ K}^{-1})$

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

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

$\Delta G^{\ominus} > 0$, therefore reverse action is spontaneous.   **[1]**
OR forward reaction is non-spontaneous
thus $CuSO_4 \cdot 5H_2O$ is more stable at 25 $^{\circ}$C.   **[1]**

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

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

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

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

Thus forward reaction is spontaneous above 103 $^{\circ}$C   **[1]**
(*i.e.* $CuSO_4 \cdot H_2O$ is more stable above 103 $^{\circ}$C).

7.   (a)   (i)   Weak acid   *[1]*
                      for a strong 0.100 $mol\,dm^{-3}$, pH would be 1.0
                      (thus acid is partially dissociated and weak).   *[1]*
                      pH of final solution closer to 13 means $pOH = 1$ **OR** there is a substantial   *[1]*
                      vertical portion of the pH curve near the end point
                      thus a strong base.   *[1]*

        (ii) $V_b = 0.100\,mol\,dm^{-3} \times \dfrac{25.0}{22.2}$.

                                                                                                       [1]

               $= 0.113\,mol\,dm^{-3}$ *(accept M as unit).*   *[1]*

        (iii) $HIn \rightleftharpoons H^+ + In^-$ (generally weak acids)   *[1]*

               In acid solution, $[H^+]$ will shift equilibrium to the left, indicator is
               predominantly present as HIn which is one colour   *[1]*

               and in basic solution, H^+ ions are removed by OH^-, shifting equilibrium to the
               right; In^- predominantly present which is another colour.   *[1]*

        (iv) $K_a = \dfrac{[H^+][In^-]}{[HIn]}$ *[1]*

               At end point intensity of HIn and In^- is about the same (where colour change
               takes place), **OR** $[HIn] = [In^-]$ *[1]*
               therefore $K_a = [H^+]$, and $pK_a = pH$.   *[1]*

        (v)   At equivalence point $pH \simeq 8$ / between 8 and 9, so use indicator of $pK_a \approx 8$.
               (Accept 9.)   *[1]*

Question 7 continued

(b) Na^+ ions are neutral cations from a strong base.   *[1]*
ethanoate ions are basic (from a weak acid)
OR $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ **OR** hydrolyses to produce weak acid +
strong base, therefore basic.   *[1]*
Since ammonium ion is a weak acid **OR** $NH_4^+ \rightleftharpoons NH_3 + H^+$ *[1]*
then the presence of a weak acid and a weak base produces (an approximately) neutral
solution.   *[1]*

Alternate answer:

The ions in sodium ethanoate solution are
• CH_3COO^- and Na^+,
• H^+ and OH^-.
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_3COO^- and NH_4^+,
• H^+ and OH^-.
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]*
Al^{3+}: weakly acidic **OR** $Al(H_2O)_6^{3+} \rightleftharpoons \left[Al(H_2O)_5(OH)\right]^{2+} + H^+$ *[1]*
The H^+ reacts with the basic solution, reducing its pH   *[1]*
OR $\left[Al(H_2O)_6\right]^{3+} + OH^- \rightarrow \left[Al(H_2O)_5(OH)\right]^{2+} + H_2O$

(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 $NH_3 = 2$ mol acid $= 0.02304$ mol   *[1]*
$M_r = 17.04$; mass $= 17.04 \text{ g mol}^{-1} \times 0.02304 = 0.3926 \text{ g}$ *[1]*
(if $M_r = 17.0$, accept 0.392 g).
$\% = \dfrac{0.3919}{2.447} \times 100 = 16.04 \%$ *[1]*

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

8. (a) $C = C$: 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]*

(b) (i) $C = C$ at 1610–1680 cm^{-1}
$C = O$ at 1680–1750 cm^{-1}
C—H at 2840–3095 cm^{-1} *[2]*
O—H at 2500–3300 cm^{-1}
(Award [2] for three correct and [1] for any two.)

(ii) CH$_3$ 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.)

(ii) 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]*

(d) (i) Optical activity is the ability to rotate the plane of polarised light (accept rotate
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]*
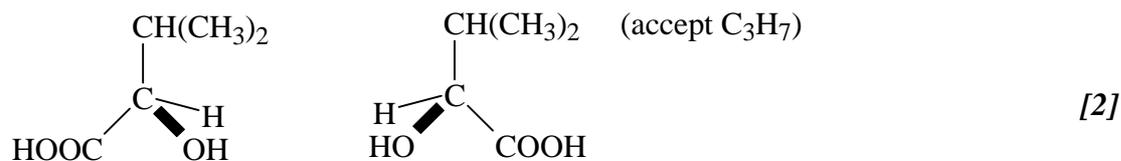
(Award only [1] if relationship is not clear.)

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

$$(-\!\!-C-\overset{\frown}{O}\!-\!H \longrightarrow -\!\!-C-O^{\ominus} + H^+)$$

[1]
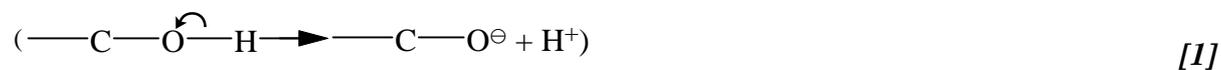
In COOH the O—H bond breaks/H^+ forms because the second O on carbon attracts e^- density from the O—H bond. *[1]*

Delocalisation stabilises the COO^- anion. *[1]*