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MARKSCHEME

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CHEMISTRY

Higher Level

Paper 2

12 pages

SECTION A

1.   (a)   (i)   Endothermic/heat absorbed/energy absorbed / increase in enthalpy / needs (a lot of) energy   *[1]*

        (ii) K_c is decreased / OWTTE.   *[1]*
Since heat is removed / since equilibrium moves to left / reverse reaction favoured.   *[1]*

        (iii) $\begin{array}{ccc} N_2 & + \quad O_2 & \rightleftharpoons 2NO \\ (1.6-x) & (1.6-x) & 2x \end{array}$ *[1]*

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$ *[1]*

$[NO] = 0.065 \ mol \ dm^{-3}$ *[1]*
(If candidate uses 1.6 *instead of* $(1.6-x)$*, which gives an answer of* 0.066*, award [2] unless it is specifically stated that an approximation has been made or* $1.6 \gg x$ *.)*

  (b)   (i) O_3: 1st order plus reasonable attempt to justify (*e.g.* double $[O_3]$ doubles rate).   *[1]*
NO: 1st order plus reasonable attempt to justify (*e.g.* triple $[O_3]$ and triple $[NO]$, rate is × 9.)   *[1]*
(Two correct orders but no reasoning, award [1].)

Rate $= k[O_3][NO]$ (*accept rate expression consistent with stated orders – ECF principle*)   *[1]*

        (ii) $0.66 \times 10^{-4} = k \times 3 \times 10^{-6} \times 10^{-6}$
$k = 2.2 \times 10^7$ *[1]* $dm^3 \ mol^{-1} \ s^{-1}$ *[1]*   *[2]*
(Apply error carried forward (ECF) from rate expression in (i). U-1 may be applied.)

        (iii)   Rate (experiment 4) $= 2.2 \times 10^7 \times 4.5 \times 10^{-6} \times 7.2 \times 10^{-6} = 7.13 \times 10^{-4}$ *[1]*

OR Rate (experiment 4) = Rate (experiment 3) $\times \dfrac{3}{2} \times \dfrac{8}{10} = 7.13 \times 10^{-4}$

(Apply ECF from rate expression in (i), must be experiment 4, units not required.)

2.   (a) C_3H_8 has higher boiling point;   *[1]*
since it has greater M_r / greater number of electrons / greater number of carbons;   *[1]*
so greater intermolecular forces / more energy needed.   *[1]*

  (b) CH_3CH_2OH has higher boiling point;   *[1]*
hydrogen bonding between molecules;   *[1]*
so more energy needed to separate molecules / so greater intermolecular forces.   *[1]*

3. (a) Acidic because H^+ donor and basic because H^+ acceptor. **[1]**

Suitable equation OWTTE involving water **[1]**

(b) O^{2-}/oxide ion (*allow* O^{-2}) **[1]**

(c) Electrical conductivity **OR** pH meter (or indicator paper) **[1]**

Strong: good conductor **OR** Strong: low pH **[1]**

Weak: poor conductor **OR** Weak: high pH **[1]**

(Allow full range indicator, do not allow litmus, use judgement on other methods.)

(d) Ratio of moles $= 60 \times 0.2 : 40 \times 0.15$ **[1]**

(acid : alkali) $=$ 2 : 1

Acid is in excess and reacts to form salt.

Moles acid : moles salt $= 1:1$ **[1]**

$$K_a = \frac{[H^+][A^-]}{[HA]} \;/\; [H^+] = K_a \frac{[HA]}{[A^-]}$$ **[1]**

$pH = 4.86$ **[1]**

*(Weak acid calculation based on excess acid giving a pH of 3.04 **[3 max]**;*

*Weak acid calculation based on total acid giving a pH of 2.89 **[2 max]**;*

*Solution based on ½ neutralisation worth **[4]**;*

Working must be shown.)

4.   (a)   Reducing agent donates/loses electrons / OWTTE.   *[1]*

   (b)   Current flow: $Al \rightarrow Ni$ *[1]*
          $Al \ominus$, $Ni \oplus$ (both)   *[1]*

   (c) $2Al + 3Ni^{2+} \rightarrow 3Ni + 2Al^{3+}$ *[2]*

          (Award [1] for correct species on correct sides of equation and [1] for correct coefficients, even if equation reversed.)

          $E^{\ominus} = +1.43\,V$ *[2]*

          (Award [1] each for sign and value. Allow −1.43 V if equation reversed – ECF principle. If signs not appropriate but value correct, award [1]. If $E^{\ominus}$ values added, award [0].)

   (d)   Seconds $= 2 \times 3600$ **OR**   7200   *[1]*

          Coulombs $= 8 \times 2 \times 3600$ **OR**   57 600   *[1]*

          $\div F$ $= \dfrac{57\,600}{96\,480}$ **OR**   0.5970   *[1]*

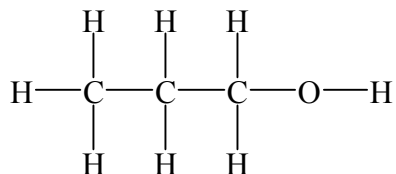 $\div 6$ $= \dfrac{57\,600}{96\,480 \times 6}$ *[1]*

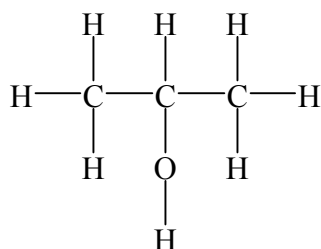   Answer $= 0.099\,50 = 0.10(00)$ *[1]*

          (Correct answer with no working, [4 max].)
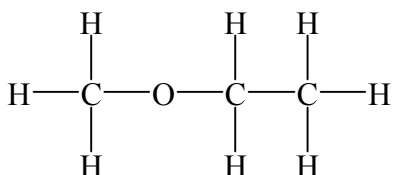
SECTION B

5.   (a)   *(If lines are shown without H atom attached, penalise once only.)*

1-propanol / propan-1-ol (I)
(do not accept propanol)

2-propanol / propan-2-ol (II)

methoxyethane (III)
(accept ether or alkoxyalkane)

$3 \times$ *[1]* $3 \times$ *[1]*

(b)   (I) partially *[1]* oxidised *[1]* to CH_3CH_2CHO *[1]*, propanal *[1]*
(if state CH_3CH_2COOH propanoic acid instead of propanal, award [1])
(II) oxidised *(if not in (I), award [1])* to CH_3COCH_3 *[1]*, propanone *[1]*
(I) or (II): orange to green   *[2]*

(c)   alkanols show bands above 3000 cm^{-1} *[1]*
III is the choice   *[1]*
since it has C–O(–O) but no –O–H   *[1]*

(d)   A is I *[1]*   3 Hs in CH_3, 2 Hs in adjacent CH_2, 2 Hs in next CH_2, 1 H in OH   *[1]*
B is II *[1]*   6 Hs in the two CH_3s, 1 H in CH, 1 H in OH   *[1]*

(e)   I and II   *[1]*
both give $CH_3CH=CH_2$ / CH_3CHCH_2 *[1]*

$CH_3CH=CH_2 + H_2$ $\rightarrow$ $CH_2CH_2CH_3$
OR $CH_3CH=CH_2 + HBr$ $\rightarrow$ $CH_3CHBrCH_3$ (or $CH_3CH_2CH_2Br$)
OR $CH_3CH=CH_2 + H_2O$ $\rightarrow$ $CH_3CHOHCH_3$ (or $CH_3CH_2CH_2OH$)
OR $CH_3CH=CH_2 + Br_2$ $\rightarrow$ $CH_3CHBrCH_2Br$

Reagents *[1]*   Product *[1]*

OR $CH_3CH=CH_2$ +high pressure, high temperature/catalyst $\rightarrow$
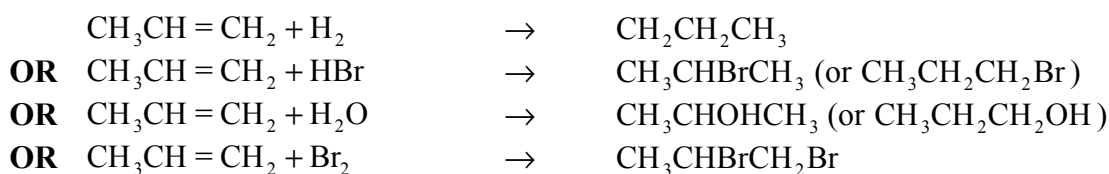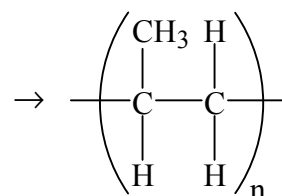
idea of polymerisation *[1]*   content of bracket *[1]*

6. (a) (i) MgO ionic   *[1]*
                SiO_2 covalent   *[1]*
                both giant structures   *[1]*
                ionic bonds strong   *[1]*
                covalent bonds strong   *[1]*
                P_4O_6 simple molecular   *[1]*
                SO_2 covalent   *[1]*
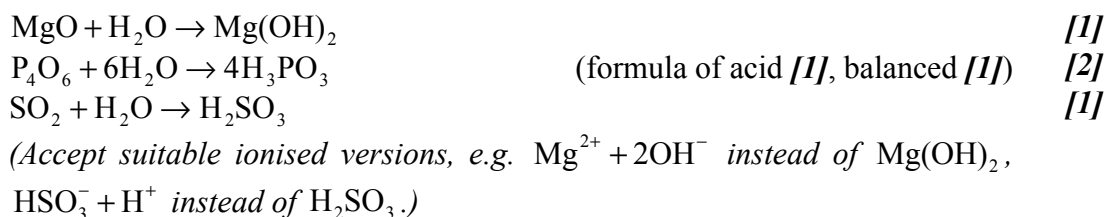   weak intermolecular forces / bonds   *[1]*   *[8]*

(ii)

Oxide	Solubility	Acidic/Alkaline/Neutral
Magnesium	Soluble	Alkaline
Silicon	Insoluble	Neutral
Phosphorus	Soluble	Acidic
Sulphur	Soluble	Acidic

   4 correct = *[3]*   4 correct = *[3]*
   3 correct = *[2]*   3 correct = *[2]*
   2 correct = *[1]*   2 correct = *[1]*   *max [6]*

$MgO + H_2O \rightarrow Mg(OH)_2$ *[1]*
$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$ (formula of acid *[1]*, balanced *[1]*)   *[2]*
$SO_2 + H_2O \rightarrow H_2SO_3$ *[1]*
(Accept suitable ionised versions, e.g. $Mg^{2+} + 2OH^-$ *instead of* $Mg(OH)_2$,
$HSO_3^- + H^+$ *instead of* H_2SO_3.)

(b) Ti $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ / [Ar] $4s^2 3d^2$ *[1]*

Variable valency / oxidation
state / OWTTE   *[1]*   removal/sharing of several electrons   *[1]*
coloured compounds   *[1]*   splitting of d orbitals, electron transitions *[1]*
complex compounds   *[1]*   accepting of electron pairs   *[1]*
catalytic activity   *[1]*   complex formation/change of valency/can
                                              easily be oxidised or reduced   *[1]*

                                              any three   *[3]*
                                              plus appropriate reason   *[3]*

7. (a) (i) $\Delta H^{\ominus}$ is positive   *[1]*
Reaction is endothermic (because products are at higher energy)   *[1]*
Bonds in reactants must be stronger than those in products (because more energy must be added than is released).   *[1]*

(ii) $\Delta G^{\ominus}$ is negative   *[1]*
because reaction is spontaneous   *[1]*
$\Delta S^{\ominus}$ is positive   *[1]*
Since $\Delta H^{\ominus}$ is positive, $\Delta S^{\ominus}$ must be positive in order to make $\Delta G^{\ominus}$ negative.   *[1]*
$(\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus})$
Products must be more disordered than reactants.   *[1]*

(iii) **Known volumes** of reactant solutions at the **same temperature** are mixed and **temperature is monitored**.   *[3]*
Mol of limiting reactant calculated from volume and **known concentration**.   *[1]*
$q = \Delta T \times \text{mass of solution} \times C_p$ *[1]*
$\Delta H = q \, \text{mol}^{-1}$ of limiting reactant   *[1]*
Use of insulated reaction vessel   *[1]*
Stir the mixture   *[1]*

Note: *[6]* **max** which **must** include:
(a) known concentration of one volume;
(b) excess or equal reacting mols of second solution;
(c) temperature change;
(d) $q = \text{mass} \times \text{specific heat capacity} \times \Delta T$

(iv) If reactants do not react completely.   *[1]*
If container is not insulated adequately, **heat will be gained from surroundings**.   *[1]*
Insulate container sufficiently.   *[1]*

(v) Reaction becomes more spontaneous as T is increased   *[1]*
less spontaneous as T is decreased.   *[1]*
$T\Delta S^{\ominus}$ term will become larger as T is raised so $\Delta G^{\ominus}$ will become more negative.   *[1]*
$T\Delta S^{\ominus}$ term will become smaller as T is lowered so $\Delta G^{\ominus}$ will become less negative (or even positive as $+\Delta H^{\ominus}$ exceeds $T\Delta S^{\ominus}$).   *[1]*
(Accept arguments based on Le Chatelier's principle.)

(b) (i) $\Delta H_{\text{reaction}} = 2(\text{A—A}) \text{ bond energy} + \text{B—B bond energy} - 4(\text{A—B}) \text{ bond energy}$ *[2]*
                         [1] for correct signs   *[1]* for correct coefficients
(Number of bonds should be clear.)

(ii) Tabulated bond energies are average values and may differ from those in specific compounds.   *[1]*
The best agreement is achieved when few bonds are broken / specific bond energies are used / for gaseous reactions.   *[1]*

8. (a) (i) $: N :: N :$ $H : \overset{..}{\underset{..}{N}} : H$ $H : \overset{..}{\underset{..}{N}} : \overset{..}{\underset{..}{N}} : H$ $H : \overset{..}{N} :: \overset{..}{N} : H$

                          H   H H

(Penalise missing lone pair once only)   *[1]* each   *[4]*

(ii) Bond angles in HNNH will be slightly larger than those in H_2NNH_2.   *[1]*
3 sets of electrons around the N atoms in HNNH (double bond, bond to H, lone pair) will be farthest apart at about $120°$ but the 4 sets in H_2NNH_2 will adopt a tetrahedral geometry with bond angles that are slightly less than $109°$ / OWTTE   *[2]*
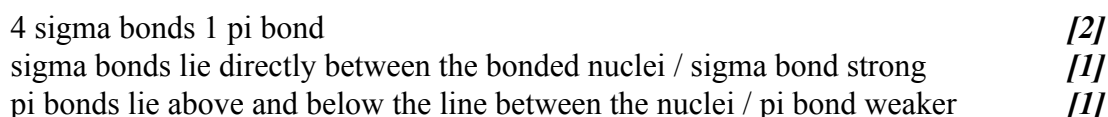
(iii) N_2 – sp hybridisation, NH_3 – sp^3 hybridisation, HNNH – sp^2 hybridisation   *[1]* each   *[3]*

(iv) HNNH has two isomers

         nonpolar   polar   *[1]* each   *[2]*
                                                                  [1] each   *[2]*

(b) (i)

4 sigma bonds 1 pi bond   *[2]*
sigma bonds lie directly between the bonded nuclei / sigma bond strong   *[1]*
pi bonds lie above and below the line between the nuclei / pi bond weaker   *[1]*
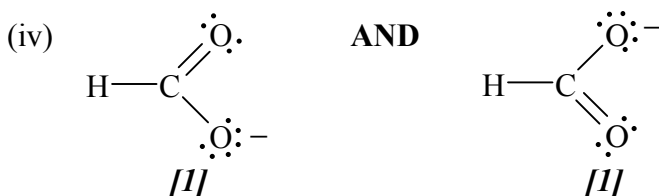
(ii) one longer than the other   *[1]*
$C = O$ shorter/extra e^- pair makes bond shorter.   *[1]*

(iii) C—O bonds of same length   *[1]*
because of delocalisation / idea of resonance.   *[1]*

(iv)

         [1]   *[1]*   *[2]*

(Negative charge omitted – no penalty, electrons on O omitted – [0].)
Intermediate bonding or other sensible alternative statement.   *[1]*
(Accept 1½ bonds / π electrons spread across C—O bonds.)