**1** (a) (i)  $2Mg + O_2 \rightarrow 2MgO$  (1) or  $Mg + \frac{1}{2}O_2 \rightarrow MgO$ (ii) Si + O<sub>2</sub>  $\rightarrow$  SiO<sub>2</sub> (1) (iii)  $S + O_2 \rightarrow SO_2$  (1) allow  $S_2$  or  $S_8$ ; not  $SO_3$  as product (3 marks) (b) (i) basic (1) not alkaline (ii)acidic (1) (2 marks) (c) (i)  $Na_2O + H_2O \rightarrow 2NaOH$  (1) allow  $Na^+OH^-$  on r.h.s. (1 mark) (ii) Ionic (1) O<sup>2</sup> ion very polarisable/strong interaction with polar water (1) reacting with water to give OH (1) (3 marks) (Total 9 marks) 2 (a) metal oxides are (more) basic than non-metal. oxides/comment on increasing basicity of oxides (1) CO<sub>2</sub> acidic (1) (3 marks) PbO amphoteric (1) Appropriate equations may be used but these must be wholly correct. (b) (i) tin +4 (1)lead +2 (1) (2 marks) (ii) Either Bond strength Pb-Cl < Sn-Cl (1) new bonds formed in the (+4) state of lead not strong enough to compensate (1) for the promotional energy of the electrons needed to form the (+4) state (1) or In tin oxidation state +4 more stable than +2 (1) In lead oxidation state +2 is more stable than +4 (1) (3 marks) (1/2 for this if no comparison with other oxidation states) Therefore lead(IV) oxidises chloride ion (to chlorine) (1) (Total 8 marks)

3 (a) The pressure which the gas exerts if it alone occupies the same volume at the same temperature (1) partial pressure of a gas in a mixture = mole fraction of gas x total pressure (1) (1 mark)  $K_p = p(PCl_3)p(Cl_2)/p(PCl_5)(1)$  no square brackets (b) (i) Or  $K_{p} = \frac{P_{PCI3} \times P_{CI2}}{P_{PCI5}}$ (1 mark) mark consequentially on (i) (ii) PCI<sub>3</sub> PCI<sub>5</sub> + Cl<sub>2</sub> mols at start 1 0 0 mols at eqm 0.60 0.40 0.40 (1)mol fraction 0.60 0.40 0.40 (1) 1.40 1.40 1.40 0.40 x2 partial pressures 0.60 0.40 1.40 1.40 1.40 =0.857=0.571=0.571(1)  $K_p = (0.571)^2 / 0.857 = 0.38 \text{ or } 0.381 \text{ (1) atm (1) but}$ 2-4 sf acceptable i.e. mols at egm (1) mols fraction partial pressures (i.e. multiply x2) substitute in  $K_p$  + answer (1) units (5 marks) (1)(c) (i) Endothermic (1) conditional on increase of temperature moves equilibrium in direction that absorbs heat (1) (2 marks) (ii)  $K_p$  increases (1) (1 mark) (i)  $K_p = p(CO_2)$  (1) (d)  $K_p = P_{CO_2}$ (1 mark) (ii) 16 (atm) (1) ignore units. Consequential on (d)(i) (1 mark)

(Total 12 marks)

Pairs up CH<sub>3</sub>CH<sub>2</sub>COOH and CH<sub>3</sub>CH<sub>2</sub>COO (a) and H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup> (1); correct identification of which is acid and which base (1)

(2 marks)

(ii)  $K_a = [CH_3CH_2COO^{-}][H_3O^{+}]/[CH_3CH_2COOH]$  (1)  $[H^{\dagger}]$  is acceptable.

(1 mark)

- (iii)  $[H^{+}] = (K_a[HA])^{1/2}$  or  $\sqrt{Ka[HA]}$  (1) =  $(1.3 \times 10^{-5} \times 0.10)^{1/2}$ =  $1.14 \times 10^{-3}$  mol dm<sup>-3</sup> (1) pH = 2.9 or 2.94, i.e. to 1 or 2 d.p. (3 marks) Consequential on the value of [H<sup>+</sup>] provided the pH resulting is between 0 and 7.
- $[H^{+}][OH^{-}] = 10^{-14} (1) = 1.14 \times 10^{-3} [OH^{-}]$ Thus  $[OH^{-}] = 10^{-14} / 1.14 \times 10^{-3} (1)$ (3 marks) = 8.77 (8.8)  $\times 10^{-12}$  mol dm<sup>-3</sup> (1) units needed (2 or 3 sf) Consequential on the answer to (iii) for [H<sup>+</sup>] .: Allow 8.71 x  $10^{-12}$  if solved using pH + pOH and pH = 2.94;  $7.9 \times 10^{-12}$  if solved using pH + pOH and pH = 2.9.
- (b)  $CH_3CH_2COO^- + H_2O \longrightarrow CH_3CH_2COOH + OH^- (1)$ Hydroxide ions make the solution alkaline (1) or propanoate ion deprotonates the water or CH<sub>3</sub>CH<sub>2</sub>COONa + H<sub>2</sub>O → CH<sub>3</sub>CH<sub>2</sub>COOH+NaOH (1) (2 marks) Explanation then must comment that acid is weak/not fully ionised
- · (c) (i) Solution that maintains almost constant pH (1) for small addition of acid or alkali (1) (2 marks)
  - (ii)  $pH = pK_a + lg [salt]/[acid]$  (1)  $= 4.9 + \lg (0.05)/(0.025)$  (1) for dividing by 2 = 5.19 or 5.2 (1).(3 marks)

If the Henderson equation is wrong but concs are divided by 2 then 1/3 max.

Or  

$$[H^{+}] = \frac{\text{Ka[acid]}}{[\text{salt}]} (1)$$

$$= \frac{1.30 \times 10^{-6} \times 0.025}{0.050} (1)$$

pH = 5.19 or 5.2 (1)

If the concns are twice what they should be, i.e. candidate does not spot the volume increase, then max (2). The pH is still 5.2, so care is needed.

(Total 16 marks)

5 (a) (i) Energy/enthalpy released (1)

When 1 mol of solid/crystal/lattice (1)

is formed from gaseous ions (1) not from 1 mol of gaseous ions

Or

Energy released per mole (1) for:

 $M^+(g)+X^-(g) \to MX$  (s) (1 for species, 1 for phases) If 'energy change' is written then must show somehow that it is exothermic

(3 marks)

(ii) Heat or enthalpy change (not energy change) when 1 mole of gaseous ions (1) is dissolved

either:

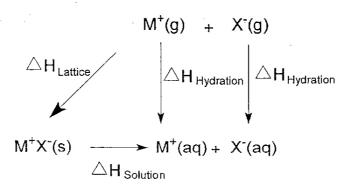
in so much water that further dilution produces no detectable heat change (1)

or

to form infinitely dilute solution (1)

(2 marks)

(b) (i)



(1) for each enthalpy change linking correct species including state symbols. Double-headed arrows scores zero

(3 marks)

(ii)  $\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$  (1)

(1 mark)

(iii) salt likely to be more soluble if  $\Delta H_{sol}$  exothermic (less endothermic) (1);

either:

both lattice energy and hydration enthalpies become less exothermic (1)

as cations increase in size (1)

but lattice energy changes less so enthalpy of solution less exothermic (1)

or:

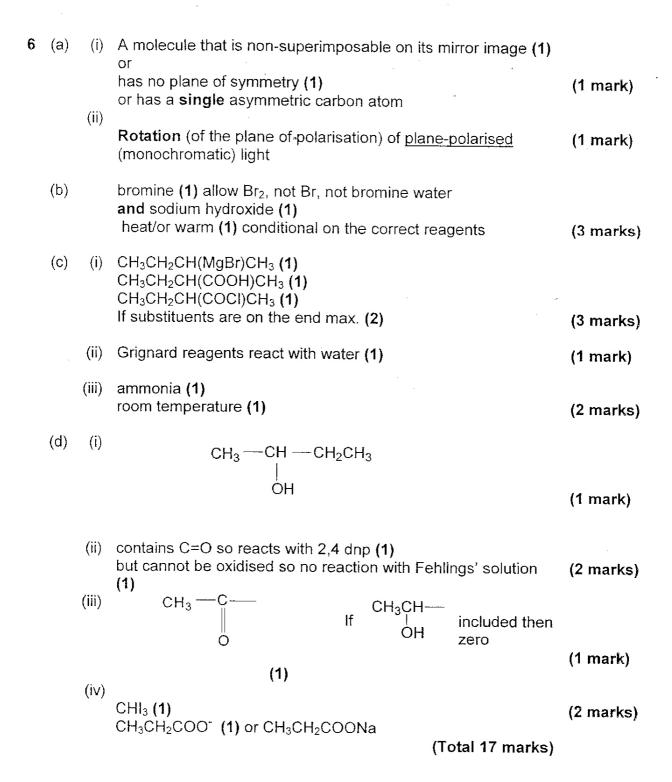
 $\Delta H_{lattice}$  is dominated by the large sulphate ion and changes little down the group (1)

so solubility depends largely on the hydration enthalpy of the cation (1)

which is less exothermic down the group as the cations get larger (1)

(4 marks)

(Total 13 marks)



**END** 

### 6245

- KMnO<sub>4</sub> (aq) in burette (1) 1 (a)
  - Pipette known volume (e.g. 25.00 cm<sup>3</sup>) of FeSO<sub>4</sub>(aq) into conical flask (1)

[Max 1 out of 2 if KMnO<sub>4</sub> in flask]

- Add (dilute) sulphuric acid (to flask) (1)
- Add KMnO<sub>4</sub> until (faint) pink colour persists (1)

[If reagents wrong way round, end point must be pink to colourless]

Record volume of KMnO<sub>4</sub> (aq) added and repeat to concordance/within 0.20cm<sup>3</sup> (1)

[Not just "repeat three times"]

(5 marks)

(i)  $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$ (b)

(1 mark)

 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ 

(1 mark)

(1 mark)

(ii)  $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ [Mark not awarded if e left in final equation]

(iii) Amount  $MnO_4 = 0.0200 \times 0.0225 = 0.00045 \text{ mol (1)}$ 

Amount  $Fe^{2+} = 5 \times 0.00045 = 0.00225 \text{ mol (1) (consequential on (b)(ii))}$ 

conc. of FeSO<sub>4</sub>(aq) = 0.00225 / 0.025 = 0.0900 mol dm<sup>-3</sup> (1) (consequential on (b)(ii))

Must be 2 to 4 sig fig

(3 marks)

 $2Fe^{3+} + Fe \rightarrow 3Fe^{2+}$  (1) (Accept  $2Fe^{3+} + 3Fe \rightarrow 3Fe^{2+} + 2Fe$ ) (c)

Either E (cell) = -0.04 - (-0.44) = +0.40 V (1)

i.e. positive therefore feasible (or answer consequential on E (cell)) (1)

Or

Equation (1)

Fe<sup>3+</sup> is the oxidised form of a redox couple with more positive EP (1)

Therefore can oxidise iron, the reduced form of other redox couple (1) (3 marks)

(Total 14 marks)

2	(a)	(i)	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(1 mark)
		(ii)	Allow single headed arrows or other suitable notation	(1 mark)
	(b)	(i)	[Mark (ii) consequentially on (i)] Covalent (1) Coordinate or dative (1)	(2 marks)
		(ii)	Deprotonation or acid-base	(1 mark)
		(iii)	[Cr(H2O)3(OH)3] or $Cr(OH)3$	(1 mark)
		(iv)	Ligand exchange or ligand substitution	(1 mark)
	(c)	(v)	<ul> <li>[Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> or [Cr(OH)<sub>x</sub> (H<sub>2</sub>O)<sub>y</sub>(NH<sub>3</sub>)<sub>z</sub>]<sup>charge</sup></li> <li>x + y + z = 6, z at least one, correct charge will be between 0 and +3, x = max 3</li> <li>d - orbitals/subshell/energy level split (in energy by ligands)/diagram to illustrate (1)</li> </ul>	(1 mark)
			Electron transitions/jumps from lower to higher energy level (1)	
			<ul> <li>Absorbs light in visible region/reference to white light (1)</li> <li>If imply or state that emission is occurring, only the first marking point is available</li> </ul>	(3 marks)
			(Total 11 marks)	

rate = k[A][B] (1) or any other where m+n=2**3** (a) rate =  $k[A]^2$  (1) rate =  $k[B]^2$  (1) (3 marks) (i) Working to show first order with respect to  $H_2$  (1) (b) Working to show second order with respect to NO (1) Overall rate equation (must be consequential) (3 marks) rate =  $k [H_2] [NO]^2$  $0.02 = k (1.0)^2 (1.0)$  or correct use of either of the other two rows of data k = 0.02/1.0 = 0.02 (1) $mol^{-2}dm^6s^{-1}$  (1) (2 marks) Consequential on (b)(i) Molecules move faster/have more kinetic energy (1) (c) More molecules / collisions have at least Eact (1) Greater proportion/fraction of collisions are successful OR more of the collisions are successful (1) (3 marks) k increases (1 mark) (d) (e) Catalyst provides an alternative route (1) With a lower activation energy (consequential on first mark) (1) Rate increases because more collisions have enough energy to overcome the lower activation energy (1) [Accept argument based on Arrhenius equation for third mark] (3 marks) (Total 15 marks)

# 4 (a) (i) Conc. sulphuric acid(1)

Conc. nitric acid (1)

[Conc. must be stated, or implied, for both acids]

(2 marks)

}-

(ii)

 $HNO_3 + H_2SO_4 \rightarrow H_2O + HSO_4^- + NO_2^+$  (1) Can be shown in two stages

Or

 $HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + 2HSO_4^- + NO_2^+$  (1)

 $NO_2$  H (1) for intermediate

I.e. curved arrow from benzene ring of electrons towards N in  $NO_2^+$  ion (1)

Intermediate correctly drawn, including positive charge (1) Curved arrow from C-H bond back into benzene ring (1)

(4 marks)

(iii) Electrophilic substitution

(1 mark)

(3 marks)

(b)

$$NO_2$$
 $NO_2$ 
 $NO_2$ 

hr

(1) (1) (1)
Vertical/right hand substituents must be shown with C to N bond
[Mark consequentially on structural formula given for
"nitrobenzene" in (a)(ii)]

- Tin / iron and concentrated hydrochloric acid/conc. HCI (c) (1) Heat (under reflux) (1) Second mark consequential on correct/"near miss" reagents
  - (2 marks)
- (d) (i) (1 mark)
  - Allow:
  - Dissolve in minimum volume (1)
    - Of boiling/hot solvent (or any specified solvent other than water) (1)
    - Filter through a heated funnel (1)
    - Cool or leave to crystallise (1)
    - Filter under suction/filter using Buchner funnel (1)
    - Wash crystals with cold solvent (1) (6 marks) NB If no solvent used, no marks available at all in part (d)(ii) (Total 19 marks)

**5** (a) Heat with Fehling's solution or heat with ammoniacal silver nitrate (1) Ketone: no change (1)

(3 marks)

Aldehyde: red ppt. or silver mirror (1)

**Alternatives** 

Allow: heat with dilute sulphuric acid and potassium

dichromate (VI) OR heat with dilute sulphuric acid and potassium

Ketone: no change (1)

Aldehyde: solution turns orange to green OR purple to colourless

**(1)** 

Allow: iodine + sodium hydroxide solution/potassium iodide +

sodium chlorate (I)

Ketone: yellow ppt. (1)

Aldehyde: no change (1)

 $K_2Cr_2O_7 / H_2SO_4 OR KMnO_4 / H_2SO_4 (1)$ (b)

Heat (under reflux) Consequential on correct reagents/OR

identify propanoic acid as the intermediate (1)

NaOH/Na<sub>2</sub>CO<sub>3</sub> + aqueous/dilute/room temp. (not 'heat') (1)

(3 marks)

(c)

Correct layout of polymer(1)

Evidence of correct continuation (1)

Correct eqn. (1)

(3 marks)

(d) CH<sub>3</sub>COCH<sub>3</sub><sup>+</sup> (1) CH<sub>3</sub>CO<sup>+</sup> (1)

CH<sub>3</sub><sup>+</sup> (1)

(3 marks)

Penalise omission of + charge once only

If m/e not stated, assume ions are listed in m/e order 58, 43 and 15

(e) Propanone has 1 peak (1)

Only one type/environment of hydrogen/proton (in a CH<sub>3</sub> group) (1)

Propanal has three peaks (1)

One in a CH<sub>3</sub>, one in a CH<sub>2</sub> and one as part of a CHO group OR other suitable justification (1)

(4 marks)

NB Answers in terms of e.g. I.R./M.S. scores zero

(Total 16 marks)

## 6246/02 Section A

1	(a)	Equation: $NH_3 + HCI \rightarrow NH_4CI \text{ or } NH_4^+CI^-$ (1) state symbols <i>not</i> required	1
		Calculation:  Amount HCl = 0.11 mol dm <sup>-3</sup> x 0.0371 dm <sup>3</sup> = 0.004081 mol (1)  Amount of NH <sub>3</sub> in 25.0 cm <sup>3</sup> = 0.004081 mol  Amount in 250 cm <sup>3</sup> = 0.04081 mol (1)  Amount of NH <sub>3</sub> in 10 cm <sup>3</sup> of $\mathbf{X}$ = 0.04081 mol (1)  [NH <sub>3</sub> ] in $\mathbf{X}$ = 0.04081 mol / 0.0100 dm <sup>3</sup> = 4.08 (4.081) mol dm <sup>-3</sup> or [NH <sub>3</sub> ] in $\mathbf{X}$ = 0.4081 mol / 0.100 dm <sup>3</sup> = 4.08 (4.081) mol dm <sup>-3</sup> (1)  Mark consequentially for processes:  1. volume of acid to moles of acid  2. multiplying by ten to get moles in 250 cm <sup>3</sup> 3. calculate amount of NH <sub>3</sub> in 10 (or 100) cm <sup>3</sup> of $\mathbf{X}$ 4. calculating concentration by dividing moles in 10 or 100 cm <sup>3</sup> of $\mathbf{X}$ by 0.01 (for 10 cm <sup>3</sup> ) or 0.1 (for 100 cm <sup>3</sup> )	4
	(b)	Graph: Axes labelled (1) pH at start between 9 and 12 (1) graph vertical at 37.1 cm³ of acid (1) pH at end point between 6 and 4 with a vertical range of 3 to 5 pH units (1) pH at 50 cm³ of acid between 1 and 3 (1)	5
		Indicator: (consequential on graph) methyl orange / methyl red / bromophenol blue / bromocresol green (1) (not phenol phthalein / thymol blue / bromothymol blue / phenol red) pK <sub>ind</sub> ±1 lies completely within the pH of the vertical range or it changes colour / working range within the pH of the vertical part of the curve (1)	2
	(c)	Add excess of solution X to copper sulphate solution / zinc sulphate solution (or add a little of the test solution to some X) (1) (blue ppt) giving deep blue solution with excess X or white ppt giving colourless solution with zinc sulphate (or equivalent with cobalt(II) chloride) (1)	
		or add excess of solution X to a suspension / solid silver chloride (1) which forms a colourless solution (1) or add any named aldehyde to a mixture of X and silver nitrate solution (1) and observe silver mirror (1)	2

Total 14 marks

### Section B

2 (a) (i) P = 24.6 / 31 (1) 0.794 / 0.794 = 1 EF is  $PF_5$  (1) F = 75.4 / 19 3.97 / 0.794 = 5  $M_r$  of EF = 126 (1) Therefore MF = EF =  $PF_5$  (1) There must be some use of the data of 126 g mol OR Mass of phosphorus in 1 mole =  $126 \times 24.6 / 100 = 31$  (1) Mass of fluorine in 1 mole =  $126 \times 75.4 / 100 = 95$  (1) Moles of phosphorus in 1 mole compound = 31/31 = 1 Mole of fluorine in 1 mole compound = 95/19 = 5 (1) MF =  $PF_5$  (1)

F P 120° OR F F

note: there must be an attempt at a 3-D drawing (i.e. one wedge and one dotted line)
Angles drawn on diagram of 90° (1) and 120° (1)

note: again it must be 3-D (again wedges and dotted lines) Name stated as octahedral (1) Angle marked / stated as 90° (1)

(b) HF has intermolecular hydrogen bonding (but others do not) (1)
Because F atom is very small / other halogen atoms / chlorine etc. radii are too large (1)
Hydrogen bonding is stronger than IMF/vdW/dipole-dipole/induced dipole-dipole/dispersion forces and so more energy required (to boil) (1)
Do not give any marks if the candidate answers in terms of strength of covalent bonds.
Do not give all 3 marks unless the candidate has expressed their ideas clearly.

Total 18 marks

4

3

3

3

5

# 3 (a) (i) Reagent: ethanoyl chloride / CH<sub>3</sub>COCI (1) Conditions step 1 anhydrous aluminium chloride/AICI<sub>3</sub> (as catalyst) or anhydrous FeCI<sub>3</sub>(1) step 3 no AICI<sub>3</sub> / catalyst or step 1 needs heating, step 3 does not (1) (ii) Reagents: potassium cyanide + named acid / potassium cyanide buffered between pH 6 to 8 / hydrogen cyanide + named base / hydrogen cyanide buffered between pH 6 to 8 / HCN + KCN (1) Names or full formulae acceptable Mechanism:

Marks awarded for:

Curly arrow from C (not the minus) of CN ion towards C of C=O (1)

Curly arrow from C=O bond to O atom (1)

Intermediate with its charge and a curly arrow from O (not the minus) to H<sup>+</sup> or to H of HCN (1)

Type: nucleophilic addition (1)

(iii) Calculation:

Amount of benzene =  $10.0 \text{ g} / 78 \text{ g mol}^{-1} = 0.1282 \text{ mol}$  (1)

Maximum amount of product = 0.1282 mol (1)

Maximum mass of product = 189 g mol<sup>-1</sup> (1) x 0.1282 mol = 24.2(3) g

Yield =  $(3.00 / 24.23) \times 100 = 12.4 \%$  (1)

Or by mole ratio

Moles benzene = 10.0/78 = 0.1282 (1)

Moles product = 3.00/189 = 0.01587 (1)

They react in 1:1 ratio (1)

Yield =  $0.01587 \times 100/0.1282 = 12.4\%$  (1)

If the erratum had not been read out, the  $M_r$  of the product would be 177 g  $mo\Gamma^1$ , giving a yield of 13.2%

Explanation: Yield low because so many / 3 steps / side reactions at each step (1)

- (b) (i) Urea has  $\delta$ + H and / or  $\delta$  O and / or  $\delta$  N atoms (1) so it can form hydrogen bonds with water (1) to  $\delta$  O and / or  $\delta$ + H in water/diagram showing charges and dotted lines(1) 3 Do not give all 3 marks unless the candidate has expressed their ideas clearly
  - (ii) Any two of:
    Lowers pH (1)
    Low % nitrogen (1)
    (high osmotic pressure) can cause scorching of foliage (1)
    leached out / very soluble (1)

Total 18 marks

3

3

1

1

 $K_{c} = [CO_{2}] [H_{2}]^{4}$ (a)  $[CH_4][H_2O]^2$  (1) Starting amounts:  $CH_4 = 10 \text{ g} / 16 \text{ g mol}^{-1} = 0.625 \text{ mol}^{-1}$ (1)  $H_2O = 54 \text{ g} / 18 \text{ g mol}^{-1} = 3.0 \text{ mol}$ Equilibrium amounts:  $CH_4 = 0.625 - \frac{1}{4} \times 2.0 = 0.125 \text{ mol}$  (1)  $H_2O = 3.0 - \frac{1}{2} \times 2.0 = 2.0 \text{ mol (1)}$  $CO_2 = 0.0 + \frac{1}{4} \times 2.0 = 0.500 \text{ mol (1)}$  $H_2 = 2.0 \text{ mol (given)}$ Equilibrium concentrations: above values ÷ 4 dm3 (1) (mark consequentially)  $[CH_4] = 0.03125 \text{ mol dm}$  $[H_2O] = 0.500 \mod dm^{-3}$  $[CO_2] = 0.125 \text{ mol dm}^{-3}$  $[H_2] = 0.50 \text{ mol dm}^{-3}$  $K_c = \frac{[CO_2]_{eq}}{[CH_4]_{eq}} \frac{[H_2]_{eq}}{[H_2O]_{eq}} = \frac{0.125 \times 0.50^4}{0.03125 \times 0.500^2}$ = 1.0 (or 1 or 1.00) (1)  $mol^2 dm^{-6}$ (1)

- (b)  $\Delta H = (-394) [(-76) + (2 \times -242)]$  (2) 1 mark for x 2, 1 mark for signs and values = + 166 (1) kJ mol<sup>-1</sup> 3
  -166 scores zero
- (c) A **catalyst** (of nickel) is used because the reaction, even at 750°C, is too slow / to speed up the reaction (1)

Then any six of the following eight points:

a temperature of 750°C is used:

- as the reaction is endothermic (1)
- a high temperature increases the value of the equilibrium constant (1)
- and so increases the equilibrium yield (1)
- a high temperature also favours a fast rate (1)
- but a temperature > 750 would be too expensive / cause engineering problems (1)

Temperature could score up to 5 but max 6 for T and P combined.

If their calculation in (b) gives an exothermic answer, mark consequentially [exothermic (1), decreases  $K_{\rho}$  (1), decreases yield (1) but faster rate(1), so 750 is compromise of fast rate and lower yield (1)]

A pressure of 30 atm is used

- even though the reaction goes from 3 to 5 gas moles / more gas moles of right of equation (1)
- causing a decrease in equilibrium yield (1)
- but a moderately high pressure is needed to push the gases through the plant (1)

Ignore any reference to rate

Pressure could score up to 3 but max 6 for T and P combined.

Do not give all 7 marks unless the candidate has expressed their ideas clearly

Total 18 marks

8

7