

1. (a) (i)  $2\text{Ca}(\text{NO}_3)_2 \rightarrow 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$   
 formulae correct (1) balance (1). Ignore any state symbols.  
 The balance mark is **not** stand-alone. 2
- (ii) steam / fizzing sound / crumbles (1)  
 solid swells up / milky liquid produced / comment about sparingly soluble  
 substance (1)  
 $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$  (1) ignore any state symbols 3
- (iii) less (1) 1
- (iv) (Cat)ion size increases down the Group / charge density decreases (1)  
 (not atom size)  
 The polarizing power of the cation decreases down the Group (1).  
 The less polarized the anion is by the cation the more difficult the nitrate is to  
 decompose (1).  
 Polarisation mark could come from ‘the less the electron cloud is distorted...’  
**or**  
 trend in cation size (1)  
 comparison of the lattice energies of the nitrate and the oxide (1)  
 balance in favour of oxide at top of group  
 and the nitrate at the bottom (1) 3
- (b) (i) same number of particles in a smaller volume / gas density increased (1) 1
- (ii) comment related to the number of molecules on each side to explain a shift to  
 l.h.s. (1) (not just ‘due to Le Chatelier...’)  
 so at higher pressure equilibrium moves to favour  $\text{N}_2\text{O}_4$  (1) 2
- (iii)  $K_p = \frac{p(\text{NO}_2)^2}{p(\text{N}_2\text{O}_4)}$   
 There must be some symbolism for pressure, and no [ ] 1
- (iv)  $(K_p = \frac{p(\text{NO}_2)^2}{p(\text{N}_2\text{O}_4)} = 48)$   
 $p(\text{NO}_2)^2 = 48 \times 0.15 = 7.2$  (1)  
 $p(\text{NO}_2) = 2.7$  (1) atm (1) accept 2.683 / 2.68 / 2.7  
 Answer and units conditional on (iii). 3

2. (a) (i) HCl: pH = 1.13  
 $\therefore [\text{H}^+] = 0.074 \text{ mol dm}^{-3}$   
 $\therefore [\text{HCl}] = 0.074 \text{ mol dm}^{-3}$  [0.074 to 0.07413] 1
- (ii) HOCl: pH = 4.23  
 $\therefore [\text{H}^+] = 5.89 \times 10^{-5} \text{ mol dm}^{-3}$  (1)  

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} \text{ (1)}$$
 $[\text{H}^+] = [\text{OCl}^-]$  (1) or implied later in calculation  
 $[\text{HOCl}] = [\text{H}^+]^2 / K_a = 0.0932 \text{ mol dm}^{-3}$  (1) 4
- (b) (i)  $[\text{H}^+] = 0.10 / 0.1047 / 0.105$  (1)  
(ii)  $\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-$  (1)  $\rightarrow$  or  $\rightleftharpoons$   
 $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^-$  ignore state symbols  
 $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$  (1) Must be  $\rightleftharpoons$   
 $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$  ignore state symbols  
(iii) second ionisation suppressed by the first ionisation (1) 4
- (c) (i) 
$$K_c = \frac{[\text{Cl}_2]^2 \times [\text{H}_2\text{O}]^2}{[\text{HCl}]^4 \times [\text{O}_2]}$$
 1
- (ii)  $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$   
equilibrium mols 0.20 0.050 (1) 0.30 and 0.30 (1)  
[ ] eq  $\div 10$  (1) 0.020 0.0050 0.030 0.030  

$$K_c = \frac{[0.030]^2 \times [0.030]^2}{[0.020]^4 \times [0.005]} = 1010 \text{ or } 1012 \text{ or } 1013 \text{ or } 1012.5$$
  
(mol<sup>-1</sup> dm<sup>3</sup>) (1) 4
- (d) (i) As reaction (left to right) is exothermic (1)  
Decrease in temperature drives equilibrium to from left to right (1) 2
- (ii) As more (gas) molecules on the left (1), equilibrium is driven from left to right (1)  
2
- (iii) A catalyst has no effect (1)  
As it only alters the rate of the reaction not the position of equilibrium / it alters the rate of the forward and reverse reactions equally (1) 2

[20]

3. (a) Still reacting / rate of forward reaction and backward reaction equal / implication that forward and backward reactions are still taking place (1)  
But concentrations constant / no macroscopic changes (1) 2
- (b) **Temp** (Increases) Left / to SO<sub>2</sub> / to endothermic / lower yield (1)  
**Press** Increases/faster (1) Right to SO<sub>3</sub> / to smaller number of molecules (1) 3
- (c) (i) Increases rate / or suitable comment on rate (1)  
Moves position of equilibrium to endothermic side / or suitable comment on equilibrium such as reasonable yield / less SO<sub>3</sub> (1)  
**Either** compromise in which the rate is more important than the position of equilibrium  
**or**  
optimum temperature for catalyst to operate  
**or**  
valid economic argument (1) 3
- (ii) Increases rate / more SO<sub>3</sub> / only needs small pressure to ensure gas passes through plant / high or reasonable yield obtained at 1 atms or at low pressure anyway (1)  
**and**  
references to economic cost against yield benefit  
e.g increase in pressure would increase yield of product but the increase in yield would not offset the cost of increasing the pressure (1) 2
- (iii) Catalyst speeds up reaction (1) 1
- (d) Vanadium (V) oxide / vanadium pentoxide / V<sub>2</sub>O<sub>5</sub> (1) 1
- (e) Any one use  
**production** of fertilizers, detergents, dyes, paints, pharmaceuticals (in) car batteries, pickling metal 1
4. (a) only partially dissociated / ionised / not fully dissociated (1)  
into H<sup>+</sup> ions / H<sub>3</sub><sup>+</sup>O / proton donor (1) 2
- (b)  $K_a = \frac{[H_3O^+][A^-]}{[HA]}$  (1) 1
- (c) (i) 9.0 to 9.4 (1) 1

[13]

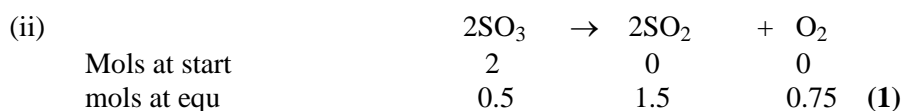
- (ii) 9.0 to 9.4 (1)  
or same answer as (c)(ii) 1
- (iii)  $pK_a = 5.6$  (1)  
 $K_a = 2.5 \times 10^{-6}$  (1) consequential 2
- (d) (i) (a solution that) resists change in pH / retains an **almost constant pH** (1)  
on addition of **small** quantities of acid or alkali (1) 2
- (ii) 5.2 to 5.8 (1)  
5.5 or 5.6 (1) or answer from (c) (iii) based on misreading scale  
of graph, eg. 4.8 2
- (e) Phenolphthalein (1)  
indicator changes colour between pH 7 and 10 this is vertical part of graph (1)  
methyl orange would change in acid / give pH between pH4 and pH6 (1)  
n. b. must be +ve statement about methyl orange 3
- (f) exothermic reaction / heat (energy) released during reaction (1)  
HCl is strong acid fully ionised (1)  
this is weak acid so some energy used for dissociation (1) 3
- (g) (i)  $pH = -\log_{(10)} [H^+]$  or in words 1
- (ii)  $1.8 \times 10^{-5} = \frac{[H^+]^2}{1}$  (1)  
 $[H^+] = \sqrt{1.8 \times 10^{-5}} = 4.24 \times 10^{-3}$  (1)  
 $pH = -\log(4.24 \times 10^{-3})$   
 $= 2.37/2.4$  (1) 2 to 4 sig. figs. 3

[21]

5. (a) (i)  $K_p = \frac{P_{SO_2}^2 \times P_{O_2}}{P_{SO_3}^2}$  (1)

[ ] no mark  
( ) OK

1



**Mark by process**

1 mark for working out mole fraction

1 mark for  $\times 10$

1 mark for correct substitution in  $K_p$  and answer

1 mark for unit

i.e.  $P_{\text{SO}_2} = \frac{1.5}{2.75} \times 10 = 5.46$

$P_{\text{O}_2} = \frac{0.7}{2.75} \times 10 = 2.73$

$P_{\text{SO}_3} = \frac{0.5}{2.75} \times 10 = 1.83$

*n.b. could show mole fraction for all 3 and then  $\times 10$  later to give partial pressure.*

$K_p = (5.46)^2 \times (2.73) / (1.83)^2 = 24.5$  (1) atm (1) 5

(b) (i) No effect (1) 1

(ii) No effect (1) 1

[8]

6. (a) (i) fraction of the total pressure generated by a gas or  
or  
pressure gas would generate if it alone occupied the  
volume  
or  
 $P_{\text{total}} \times \text{mol fraction}$  (1) 1

(ii)  $K_p = \frac{p(\text{CO}) \times p(\text{H}_2)^3}{p(\text{CH}_4) \times p(\text{H}_2\text{O})}$  (1) not [ ] 1

(iii) Increase in total pressure will result in less product  
molecules in the equilibrium mixture / equilibrium  
moves to left (1)  
because more molecules on product side of the equilibrium  
than on left (1) 2

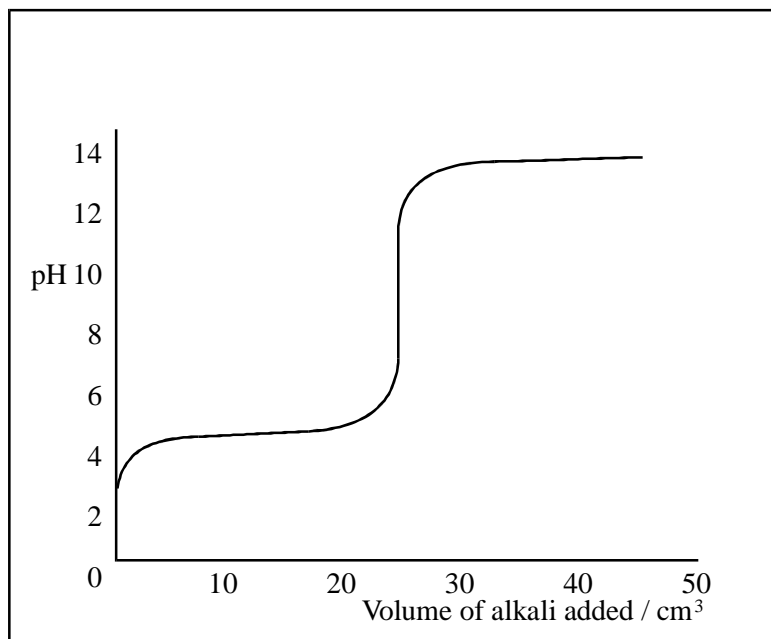
(b) (i) No change (1) 1

- (ii)  $K_p$  increase (1) 1
- (iii) No change (1) 1
- (c) (i)  $K_p = \frac{1}{p(\text{CH}_4)}$  (1) 1
- (ii)  $9.87 \times 10^{-3} \text{ kPa}^{-1} / 9.87 \times 10^{-6} \text{ Pa}^{-1}$  consequential on (i) (1) 1  
*Allow 3 – 5 sig fig*
- (iii) equilibrium has moved left in favour of gas (1)  
 exothermic going left to right/in the forward direction / as  
 written (1) *Stand alone* 2
- (iv) Answer yes or no with some sensible justification (1)  
 e.g. No the costs would not justify the amount produced 1

[12]

7. (a) Few molecules dissociate (into protons) / partially dissociated / ionised (1) 1  
*Not fully dissociated scores zero*
- (b) Maintains an **almost** constant pH / resists change in pH (1)  
 with the addition of **small** amounts of acid or alkali (1) 2

(c)



starting pH (1) at 2.8

endpoint (1) vertical between 6 and 11 including 7-10

vertical (1) at 25 cm<sup>3</sup>

general shape (1) finish above 12

4

(d) Almost horizontal area marked on graph (1)

1

(e) (i) 
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad (1)$$

or

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad (1)$$

1

(ii) pH = pK<sub>a</sub> at half way to neutralisation point = 12.5 cm<sup>3</sup> (1)

This could be shown on the graph

because pH = pK<sub>a</sub> when [CH<sub>3</sub>COO<sup>-</sup>] = [CH<sub>3</sub>COOH] (1)

2

[11]

8. (a) The marks are for:
- writing the expression for K
  - substituting correctly
  - calculating  $p(\text{SO}_3)$
  - correct generation of the ratio
  - calculation of the ratio to give answer which rounds to 95 t

$$K_p = p\text{SO}_3^2 / p\text{SO}_2^2 \times p\text{O}_2 (= 3.00 \times 10^4) \text{ (1)}$$

$3.00 \times 10^4 = p\text{SO}_3^2 / 0.1 \times 0.1 \times 0.5 \text{ (1)}$  if no expression for  $K_p$  is given this correct substitution can score 2 marks

$$p\text{SO}_3^2 = 150$$

$$p\text{SO}_3 = 12.25 \text{ (1)}$$

$$\text{Ratio of SO}_3 = \frac{12.25 \times 100\%}{(12.25 + 0.1 + 0.5)} \text{ (1)} = 95\% \text{ (1)} \quad 5$$

- (b) (i) The marks are for
- Recognizing the existence of hydrogen bonds ( between molecules) **(1)**
  - That each molecule can form more than one hydrogen bond because of the two OH (and two S=O groups) / or a description of hydrogen bonds in this case / or a diagram showing the hydrogen bonds **(1)**
  - That hydrogen bonds make for strong intermolecular forces (and hence high boiling temperature) which requires higher **energy** to break / separate molecules **(1)** 3
- (ii) If water is added to acid heat generated boils and liquid spits out **(1)**  
if acid added to water the large volume of water absorbs the heat generated (and the mixture does not boil) **(1)** 2
- (c) (i)  $\text{pH} = -\log_{10} (0.200) = 0.70 \text{ (1)}$   
allow 0.7 or 0.699 1
- (ii) realising that the **first** ionisation / dissociation of sulphuric and that of HCl are **both** complete **(1)**  
that the second ionisation of sulphuric is suppressed by the  $\text{H}^+$  from the first **(1)**  
little contribution from 2nd ionisation so reduces the pH  
very little / increases the  $[\text{H}^+]$  very little **(1)** 3



- (d) (i) Lead equations 1 mark  
 $\text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{H}^+ + 2\text{e}^-$  (1)  
 or  
 $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$   
 Lead(IV) oxide equations 2 marks  
 $\text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$   
 or  
 $\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$   
 Species (1) balancing (1) 3

- (ii)  $\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$  (1) 1

[18]

9. (a) (i)  $\text{pH} = -\log_{10} [\text{H}^+] / \text{pH} = -\lg [\text{H}^+]$  (1) 1

- (ii)  $K_{\text{W}} = [\text{H}^+] [\text{OH}^-]$  or  $K_{\text{W}} = [\text{H}_3^+\text{O}] [\text{OH}^-]$  (1) 1

- (b) fully ionised / fully dissociated / almost completely ionised (1) 1

- (c) (i) 0.70 (or 0.699) (1) 1

- (ii)  $[\text{H}^+] = K_{\text{W}} / [\text{OH}^-] = 1.25 \times 10^{-14}$  (1)  
 $\text{pH} = 13.9$  or  $13.90$  (1) 2

- (d) (i)  $K_{\text{a}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$  (1) 1  
 allow  $[\text{H}_3^+\text{O}]$

- (ii)  $[\text{H}^+] = \sqrt{K_{\text{a}} \times [\text{HA}]}$  (1) = 0.00474 (1)  
 $\text{pH} = 2.32 / 2.33$  (1) 3

(e)  $[H^+] = \frac{K_a[HA]}{[A^-]}$  (1)

$[H^+] = (5.62 \times 10^{-5} \times 0.3) / 0.6 = 0.0000281 / 2.81 \times 10^{-5}$  (1)

pH = 4.55 (1) 3

Or

$pH = pK_a + \log \frac{[A^-]}{[HA]}$

$= -\log_{10} (5.62 \times 10^{-5}) + \log_{10} \frac{[0.600]}{[0.300]} = 4.55$

If initial error in statement of  $[H^+]$  or Henderson equation max 1

[13]

10. (a) (i)  $K_c = [SO_3]^2 / [SO_2]^2 [O_2]$  (1) 1

(ii)  $\frac{0.2}{30} \quad \frac{0.1}{60} \quad \frac{1.8}{60}$

$= 3.33 \times 10^{-3} \quad 1.67 \times 10^{-3} \quad 0.03$  (1)

$K_c = \frac{(0.03)^2}{(3.33 \times 10^{-3})^2 \times 1.67 \times 10^{-3}} = 4860 \text{ or } 4.86 \times 10^{-4}$  (1)

$\text{mol}^{-1} \text{ dm}^3$  (1) 3

(b) (i)  $K_c$  decreases (1) 1

(ii) shifts to left / in reverse (1) 1

(c) (i) no effect (1) 1

(ii) no effect (1) 1

(d) (i)  $K_p = pSO_3^2 / pSO_2^2 \times pO_2$  (1) penalise square brackets 1

(ii) Total number of moles (1) consequential on a (ii)

$SO_2 = 0.0952(4)$ ;  $O_2 = 0.0476$  (2);  $SO_3 = 0.857$  (1) (1) 2

(iii) Partial pressures:  $SO_2 = 0.190$  (5) atm;  $O_2 = 0.0952$  (4) atm;

$SO_3 = 1.71$ (4) atm (1) i.e. multiply answer in (ii) by 2 1

(iv)  $1.714^2 / 0.1905^2 \times 0.09524 = 850$  (1)  
 $\text{atm}^{-1}$  (1) 2

[14]

11. (a) (i) Gases have much higher entropies than solids as there are many more ways of arranging the entities / less ordered / more random(ness)  
*OR reverse argument* (1)  
 $\text{ZnCO}_3$  has more atoms/is more complex than  $\text{ZnO}$  (1) 2

(ii)  $\Delta S^\ominus_{\text{system}} = (+43.6) + (+213.6) - (+82.4)$   
 $= +174.8 / 175 \text{ J mol}^{-1} \text{ K}^{-1}$   
*method* (1)  
*answer, sign and units* (1)  
*Correct answer, sign and units with no working* (2) 2

(b)

As printed	Amended
$\Delta S^\ominus_{\text{surroundings}} = \frac{-\Delta H}{T}$	$\Delta S^\ominus_{\text{surroundings}} = \frac{-\Delta H}{T}$
OR $= \frac{-(+464.5 \times 10^3)}{298}$ (1)	OR $= \frac{-(+71.0 \times 10^3)}{298}$ (1)
$= -1560 / 1559 \text{ J mol}^{-1} \text{ K}^{-1}$	$= -238(.3) \text{ J mol}^{-1} \text{ K}^{-1}$
<i>answer, sign and units</i> (1)	<i>answer, sign and units</i> (1)

ONLY accept 3 or 4 SF 2  
*IF correct answer, sign and units with no working* (1)

(c) (i)

$\Delta S^\ominus_{\text{total}} = +174.8 - 1558.7$	$= -63.5 / 64 / 63 / 63.2 / 63.4 \text{ J mol}^{-1} \text{ K}^{-1}$
$= -1384 / -1380 \text{ J mol}^{-1} \text{ K}^{-1}$	
$IF + 174.8 - 1560$	
$= -1385(.2)$	
$= -1385 / 1390 \text{ J mol}^{-1} \text{ K}^{-1}$	
$IF + 174.8 - 1559$	
$= -1384 \text{ J mol}^{-1} \text{ K}^{-1}$	

ONLY penalise incorrect units OR no units in (a)(ii), (b) and (c)(i) *once* 1

- (ii) Natural direction is right to left /reverse as  $\Delta S^\ominus_{\text{total}}$  /**total entropy change**

is negative / less than zero. 1

MUST be consistent with (i)

- (d) (i)  $K_p = p_{\text{CO}_2}$  ((g) eqm) 1  
(ii) Increase temperature / reduce pressure (1)  
Decreases  $\Delta S^\ominus_{\text{surroundings}}$  (negative) and hence increases  $\Delta S^\ominus_{\text{total}}$  / Le Chatelier's principle applied (i.e increasing temperature, reducing pressure) (1) 2

[11]

12. (a) (i) Pairs up  $\text{CH}_3\text{CH}_2\text{COOH}$  and  $\text{CH}_3\text{CH}_2\text{COO}^-$   
and  $\text{H}_2\text{O}/\text{H}_3\text{O}^+$  (1); correct identification of which is acid and which base (1) 2
- (ii)  $K_a = [\text{CH}_3\text{CH}_2\text{COO}^-] [\text{H}_3\text{O}^+] / [\text{CH}_3\text{CH}_2\text{COOH}]$  (1) 1  
 *$[\text{H}^+]$  is acceptable.*
- (iii)  $[\text{H}^+] = (\text{Ka}[\text{HA}])^{1/2}$  or  $\sqrt{\text{Ka}[\text{HA}]}$  (1) =  $(1.3 \times 10^{-5} \times 0.10)^{1/2}$   
=  $1.14 \times 10^{-3} \text{ mol dm}^{-3}$  (1) pH = 2.9 or 2.94, i.e. to 1 or 2 d.p. (1) 3  
Consequential on the value of  $[\text{H}^+]$  provided the pH resulting is between 0 and 7.
- (iv)  $[\text{H}^+][\text{OH}^-] = 10^{-14}$  (1) =  $1.14 \times 10^{-3} [\text{OH}^-]$   
Thus  $[\text{OH}^-] = 10^{-14} \times 10^{-3}$  (1)  
=  $8.77 (8.8) \times 10^{-12} \text{ mol dm}^{-3}$  (1) units needed (2 or 3 sf)  
*Consequential on the answer to (iii) for  $[\text{H}^+]$*   
Allow  $8.71 \times 10^{-12}$  if solved using pH + pOH and pH = 2.94;  
 $7.9 \times 10^{-12}$  if solved using pH + pOH and pH = 2.9. 3
- (b)  $\text{CH}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOH} + \text{OH}^-$  (1)  
Hydroxide ions make the solution alkaline (1) or propanoate ion deprotonates the water  
or  $\text{CH}_3\text{CH}_2\text{COONa} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NaOH}$  (1)  
Explanation then must comment that acid is weak/not fully ionised 2
- (c) (i) Solution that maintains almost constant pH (1)  
for **small** addition of acid or alkali (1) 2

- (ii)  $\text{pH} = \text{pK}_a + \lg [\text{salt}]/[\text{acid}]$  (1)  
 $= 4.9 + \lg (0.05)/(0.025)$  (1) for dividing by 2  
 $= 5.19$  or  $5.2$  (1). 3

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

Or

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

$$= \frac{1.30 \times 10^{-5} \times 0.025}{0.050} \text{ (1)}$$

$\text{pH} = 5.19$  or  $5.2$  (1)

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

[16]

13. (a)  $\text{pH} = -\lg [\text{H}^+(\text{aq})]$   
 OR  $[\text{H}^+(\text{aq})] = 10^{-\text{pH}} / 10^{-9.6} = 10^{-9.6}$  (method) (1)  
 $= 2.5(1) \times 10^{-10} \text{ mol dm}^{-3}$  (2) 3

(b) (i)  $\text{K}_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$  1

(ii)  $[\text{OH}^-(\text{aq})] = \frac{\text{K}_w}{[\text{H}^+(\text{aq})]}$   
 $= \frac{1.0 \times 10^{-14}}{2.51 \times 10^{-10}}$   
 $= 3.98 / 4(.0) \times 10^{-5} \text{ mol dm}^{-3}$  1

(iii)  $[\text{Ca}(\text{OH})_2(\text{aq})] = 0.5 \times 3.98 \times 10^{-5}$   
 $= 1.99 / 2(.0) \times 10^{-5} \text{ mol dm}^{-3}$  1

(iv)  $= 1.99 / 2(.03) \times 10^{-5} \times 74$   
 $= 0.00147 \text{ (g dm}^{-3}\text{) MUST be to 3 SF}$  1

(v) Due to reaction with carbon dioxide in the air / temperature differences 1

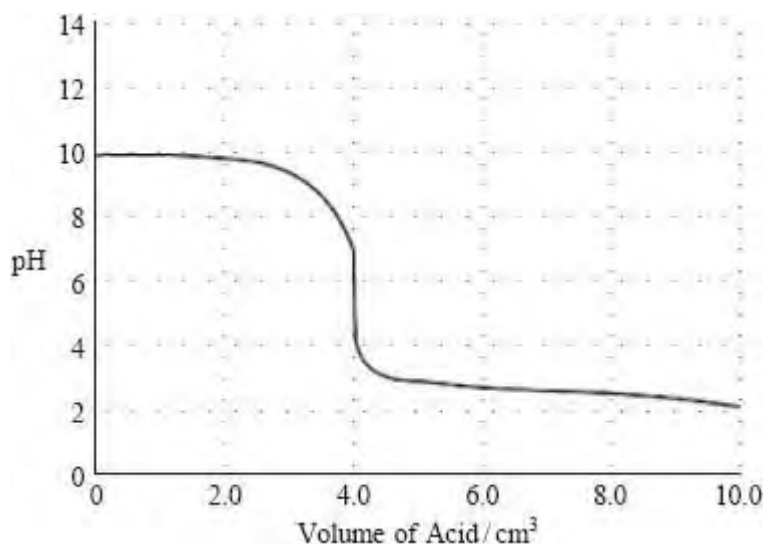
(c) (i) pH = 3(.0) *Penalise if more than 2 SF* 1

(ii) Amount of  $\text{Ca(OH)}_2 = \frac{100 \times 1.99 \times 10^{-5}}{1000}$   
 $= 1.99 \times 10^{-6} \text{ mol (1)}$

$\therefore$  Amount of HCl =  $\frac{2 \times 100 \times 1.99 \times 10^{-5}}{1000}$   
 $= 3.98 \times 10^{-6} \text{ mol (1)}$

$\therefore$  Volume of HCl =  $\frac{1000 \times 2 \times 100 \times 1.99 \times 10^{-5}}{1000}$   
 $= 4(.0) / 3.98 \text{ cm}^3 \text{ OR } 4(.0) / 3.98 \times 10^{-3} \text{ dm}^3 \text{ (1)}$  3

(iii)



**Vertical** portion of the graph (between pH 7 and 4) at about 4 cm<sup>3</sup> (1)  
*Correct initial and finishing pH (9–10 and 3) and general shape (1)* 2

(iv) Phenolphthalein changes colour outside pH range of end point/ pH range of phenolphthalein is too high. 1

[15]

14. (a) (i)  $\text{NH}_3$  base and  $\text{NH}_4^+$  acid (1)  
 $\text{H}_2\text{O}$  acid and  $\text{OH}^-$  base (1)  
*OR*  
*linking (1)*  
*acid and base correctly identified (1)* 2

- (ii) Starting pH of (just above) 11 (1)  
 Graph showing vertical line between pH 4 and 6  
 With vertical section 3–5 units in length (1)  
 at a volume of HCl of 20 cm<sup>3</sup> (1)  
 Final pH of between 1 and 2 (1) 4
- (iii) Named indicator consequential on vertical part of their graph (1)  
 Because **all** of its range is **within** the vertical part of the graph /  
 $pK_{\text{ind}} \pm 1$  is within vertical part of graph / it changes colour  
**completely**/ stated colour change (MO: yellow – red; BB: blue –  
 yellow; PP: pink – colourless) within the pH of the vertical part of  
 the graph (1) 2
- (b) (i)  $K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{NO}_2^-]}{[\text{HNO}_2]}$   
*square brackets essential* 1
- (ii)  $[\text{H}^+] = [\text{NO}_2^-]$  or  $[\text{H}^+]^2 = K_a \times [\text{HNO}_2]$  (1)  
 $[\text{H}^+] = \sqrt{K_a \times 0.12} = 0.00751 \text{ mol dm}^{-3}$  (1)  
 $\text{pH} = -\log [\text{H}^+] = 2.12/2.1$  (1)  
 ALLOW any correct conversion of  $[\text{H}^+]$  into pH provided the  
 answer is less than 7 3
- (iii) Moles  $\text{NaNO}_2 = 1.38/69 = 0.020$  (1)  
 $[\text{NO}_2^-] = 0.020 / 0.10 = 0.20 \text{ (mol dm}^{-3}\text{)}$   
 $[\text{H}^+] = \frac{K_a [\text{acid}]}{[\text{salt}]} = \frac{4.70 \times 10^{-4} \times 0.120}{0.20} = 2.82 \times 10^{-4}$  (1)  
 $\text{pH} = -\log 2.82 \times 10^{-4} = 3.55 / 3.6 / 3.5$  (1) 4
- (iv) In a buffer both [acid] and [salt] must be large compared to the  
 added  $\text{H}^+$  or  $\text{OH}^-$  ions (1)  
 but in  $\text{NaNO}_2$  alone [  $\text{HNO}_2$  ] is very small (1)  
 OR  
 to remove both  $\text{H}^+$  and  $\text{OH}^-$  there must be a large reservoir of  
 both  $\text{NO}_2^-$  ions and  $\text{HNO}_2$  molecules (1)  
 which there are a solution of  $\text{NaNO}_2$  and  $\text{HNO}_2$  but not in  $\text{NaNO}_2$   
 alone (1) 2

15. (a) Pressure *NOT* partial pressure )  
intensity or change of colour ) *Any one*  
volume ) 1
- (b)  $K_c = [\text{NO}_2(\text{g})]^2 / [\text{N}_2\text{O}_4(\text{g})]$   
State symbols required 1
- (c) Mol  $\text{NO}_2$  at equilibrium =  $0.0120 / 1.20 \times 10^{-2}$  (1)  
 $K_c = (0.0120)^2 \div (0.0310)$   
=  $4.6 / 4.65 \times 10^{-3}$  (1) mol  $\text{dm}^{-3}$  (1) 3
- (d) (i) Amount of  $\text{NO}_2$  reduced 1  
(ii) No effect 1
- (e) As  $K_c$  is bigger, more  $\text{NO}_2$  is produced so heat helps forward reaction /  
by Le Chatelier's principle reaction goes forward to use up heat /  
as temperature increases  $\Delta S_{\text{total}}$  must be more positive so  $\Delta S_{\text{surroundings}}$   
(=  $-\Delta H/T$  must be less negative) 1
- (f) Positive / + with some attempt at explanation (1)  
1 mol / molecule gas  $\rightarrow$  2 mol / molecule gas / products more disordered  
than reactants (1) 2
- (g)  $\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$  OR  $\frac{-\Delta H \times 1000}{T}$  1
- (h)  $\Delta S_{\text{total}}$  is positive as reaction occurs (1)  
So  $\Delta S_{\text{system}}$  must be more positive than  $\Delta S_{\text{surroundings}}$  is negative (1) 2
16. (a) (i)  $\text{pH} = -\log_{(10)} [\text{H}_3\text{O}^+]$  (1)  
OR  $[\text{H}^+]$  instead of  $[\text{H}_3\text{O}^+]$  applied throughout 1  
(ii)  $[\text{H}_3\text{O}^+]$  greater than 1 (mol  $\text{dm}^{-3}$ ) 1

[13]



- (b) (i)  $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$  (1)  
 $[\text{H}_3\text{O}^+] = 1.14 \times 10^{-3} \text{ mol dm}^{-3}$  (1)  

(ii) Start at the same pH as in (i) (1)  
Graph showing vertical at 25 cm<sup>3</sup> (1)  
vertical section 3–5 units in length with midpoint around pH 8 (1)  
general shape correct including buffer zone and final pH not > 13 (1) 4
- (iii) pH = pK
- <sub>a</sub>
- 1

[10]

17. (a) Pressure exerted by the gas if it alone occupied the same volume at the same temperature/mole fraction × total pressure 1
- (b) (i)  $K_p = \frac{p(\text{N}_2)p(\text{O}_2)}{p(\text{NO})^2}$  1
- (ii) Correct number of moles (1)  
Correct mole fractions (1)  
Correct partial pressures (1)  
 $2.45 \times 10^3$  (1) ACCEPT 2–4 SF 4
- (c)  $K_p$  increases (1)  
Equilibrium moves to r.h.s. (1)  
which is the exothermic direction (1) 3
- (d) (i)  $K_p = p(\text{Ni}(\text{CO})_4) / p(\text{CO})^4$  1
- (ii) High partial pressure *with some reason* (1)  
so the pressure Ni(CO)<sub>4</sub> increases to keep K<sub>p</sub> constant. (1) 2

[12]

18. (a) (i) Methanol is the biggest/ most complex molecule / greatest  $M_R$  /most atoms/most electrons 1
- (ii)  $\Delta S_{\text{system}} = 239.7 - 197.6 - 2(130.6)$   
 $= -219.1 / -219 \text{ J mol}^{-1}\text{K}^{-1}$   
 Method (1)  
 answer + units (1) 2
- (iii) yes as 3 molecules  $\rightarrow$  1 *OR* yes as (2) gases  $\rightarrow$  a liquid 1
- (iv)  $\Delta S_{\text{surr}} = -\Delta H/T$  (stated or used) (1)  
 $= -(-129/ 298) = +0.433 \text{ kJ mol}^{-1} \text{ K}^{-1} / +433 \text{ J mol}^{-1} \text{ K}^{-1}/+ 432.9$  (1)  
 -1 for wrong units/ no units / more than 4 SF  
 -1 for wrong sign/ no sign 2
- (v)  $\Delta S_{\text{total}} = -219.1 + 433 = +213.9 / +213.8 \text{ J mol}^{-1} \text{ K}^{-1}/ +214 \text{ J mol}^{-1} \text{ K}^{-1}/$   
 $+0.214 \text{ kJ mol}^{-1}\text{K}^{-1}$  (1)  
**Positive so possible (1)** 2
- (b) (i) Temperature  
 Faster at 400°C (1)  
 even though yield is lower (1)  
Pressure  
 Higher pressure improves yield of methanol (1)  
 Higher pressure increases rate (1)  
**Maximum 3** 3
- (ii) Not in same phase as reactants. *ALLOW state instead of phase* 1
- (iii)  $K_p = p(\text{CH}_3\text{OH})/p(\text{CO}) \times p(\text{H}_2)^2$  1
- (iv) Partial pressure of methanol =  $200 - 55 - 20 = 125 \text{ atm}$  (1)  
 $K_p = (125)/55 \times 20^2$   
 $= 5.68 \times 10^{-3} / 5.7 \times 10^{-3} \text{ atm}^{-2}$  (1) 2
- (c) (i) Number of molecules / fraction of molecules with energy  $\geq E_A$  /number of molecules which have enough energy to react. 1
- (ii) Vertical line / mark on axis to show value to the left of line  $E_A$  1
19. (i) Weak acid is dissociated to a small extent/slightly dissociated/ ionised/few molecules dissociate  
*ALLOW* partial dissociation  
*NOT* 'not fully dissociated'. 1

[17]

(ii)  $K_a = \frac{[H^+][C_4H_9COO^-]}{[C_4H_9COOH]}$  OR  $[H_3O^+]$  for  $[H^+]$  1

(iii)  $K_a = [H_3O^+]^2 / [acid]$  OR  $[H_3O^+] = \sqrt{K_a [acid]}$  (1)  
 $[H_3O^+] = 1.23 \times 10^{-3}$  (1) – dependent on 1<sup>st</sup> mark  
 pH = 2.91/2.92 (1) ACCEPT 2.9 1 or 2 d.p.  
 Correct answer with working (3)  
 Correct answer with no working (1)  
 ALLOW TE only if pH below 7 3

(iv) starting pH 2.9 ALLOW starting in 2<sup>nd</sup> or 3<sup>rd</sup> boxes above pH 2 (1)  
 consequential on (iii)  
 pH range vertical max 6 to 12 min 7–10 (1)  
 Equivalence point at 25cm<sup>3</sup> (1)  
 General shape of curve **and** finish at pH between 12–13 (1) –  
 and end in 1<sup>st</sup> three boxes above 12, extending to 40–50 cm<sup>3</sup>  
 If drawn wrong way round **2 max** ie equivalence point (1) and  
 vertical drop (1) marks can be awarded 4

(v) Thymol blue (1) – Consequential on (iv)  
 (Completely) changes colour within vertical portion/the working  
 range of the indicator is within the vertical portion /  $pK_{ind} \pm 1$  in  
 vertical position /  $pK_{ind}$  in centre of vertical position (1) 2

[11]

20. Penalise **units** only once in this question

(a)  $(2 \times 192.3) - [191.6 + (130.6 \times 3)]$  (1)  
 $= -198.8 / 199 \text{ J mol}^{-1} \text{ K}^{-1}$  (1) 2

(b)  $\frac{-92.2 \times 1000}{298} - \frac{-92.2}{298} - \Delta H / T$  (1)  
 $= +309(.4) \text{ J mol}^{-1} \text{ K}^{-1} / +0.309(4) \text{ kJ mol}^{-1} \text{ K}^{-1}$  (1) 2

(c) (i)  $-198.8 + 309 = +110 \text{ J mol}^{-1} \text{ K}^{-1}$  (3 SF)  
 OR  
 $-198.8 + 309.4 = +111 \text{ J mol}^{-1} \text{ K}^{-1}$  (3 SF)  
 [Do not penalise missing + sign if penalised already in (b)]  
 NOT 4SF. Penatise SF only once on paper 1

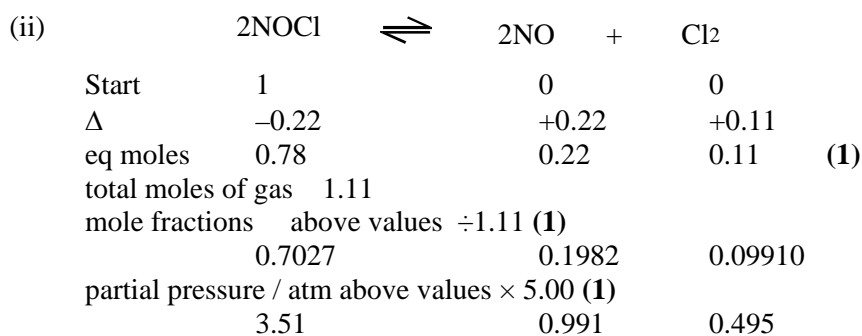
(ii) Yes, as  $\Delta S_{total}$  is positive / total **entropy change** 1

- (d) (i) Higher T makes  $\Delta S_{\text{surroundings}}$  decrease (so  $\Delta S_{\text{total}}$  is less positive) 1
- (ii) Cost (of energy) to provide compression/ cost of equipment to withstand high P/ maintenance costs. *NOT* safety considerations alone 1
- (iii) Different phase/state (to the reactants) 1

[9]

21. (a) (i)  $K_p = p(\text{CO}_2)$  allow without brackets, IGNORE p [ ] 1
- (ii) 1.48 (atm)  
 Penalise wrong unit  
 Answer is consequential on (a) (i) e.g.  $\frac{1}{1.48}$  must have  $\text{atm}^{-1}$  1

- (b) (i)  $K_p = \frac{p(\text{Cl}_2) \times p(\text{NO})^2}{(p(\text{NOCl}))^2}$  allow without brackets, penalise [ ] 1



$$K_p = \frac{0.495 \text{ atm} \times (0.991 \text{ atm})^2}{(3.51 \text{ atm})^2} \quad (1)$$

$$= 0.0395 / 0.0394 \text{ atm} \quad (1)$$

range of answers 0.0408 / 0.041  $\rightarrow$  0.039 / 0.0392 NOT 0.04

ACCEPT  $\geq 2$  S. F

Correct answer plus some recognisable working (5)

Marks are for processes

- Equilibrium moles
- Dividing by total moles
- Multiplying by total pressure
- Substituting **equilibrium** values into expression for  $K_p$

5

Calculating the value of  $K_p$  with correct consequential unit.

(iii) As the reaction is endothermic – *stand alone* (1)  
 the value of  $K_P$  will increase (as the temperature is increased) - (1)  
*consequential on 1<sup>st</sup> answer (if exothermic (0) then  $K_P$  decreases (1))*  
*For effect on  $K_P$  mark, must have addressed whether reaction is*  
*endothermic or exothermic* 2

(iv) **Because** (as the value of  $K_P$  goes up), the value of  
 $pCl_2 \times (pNO)^2 / (pNOCl)^2$  (the quotient) **must also** go up (1)  
 and so the position of equilibrium moves to the right – *stand alone* (1)  
**But** mark *consequentially* on change in  $K$  in (iii)  
*If “position of equilibrium moves to right so  $K_p$  increases” (max 1)* 2  
*IGNORE references to Le Chatelier’s Principle*

[12]

22. (a)  $CH_3COOH$  labelled as base and linked to  $CH_3COOH_2^+$  labelled  
 (conjugate) acid (1)  
 $H_2SO_4$  labelled acid and linked to  $HSO_4^-$  labelled (conjugate) base (1)  
*If acids and bases correct but not clearly or correctly linked 1 (out of 2)*  
*Just link but no identification of acids and bases (0)* 2

(b) (i) (pH) more than 7 / 8-9 (1)  
 Indicator: phenolphthalein ALLOW thymolphthalein OR thymol blue  
*(mark consequentially on pH) (1)* 2  
*Mark consequentially on pH but if pH7 do not allow either methyl*  
*orange or phenolphthalein*

QWC\*(ii) As  $OH^-$  / base removes  $H^+$  ions /  $\Delta H_{neut}$  is per mole of  $H_2O$  produced / (1)  
 $H^+ + OH^- = H_2O$   
 the equilibrium shifts to the right (1)  
 and so **all** the ethanoic acid reacts (not just 1% of it) (1)  
 OR  
 Endothermic (OH) bond breaking (1)  
 is compensated for (1)  
 by exothermic hydration of ions (1)  
 OR  
 $\Delta H$  for  $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+ = +2kJ\ mol^{-1}$  / almost zero /  
 very small (1)  
 $\therefore \Delta H_{neut} [CH_3COOH] = +2 + \Delta H_{neut} [HCl]$  (1)  
 $\approx$  the same (for both acids) (1)  
 OR  
 $\Delta H_{neut}$  is per mole of  $H_2O$  produced (1)  
 (heat) energy required for full dissociation (of weak acid) (1)  
**so**  $\Delta H_{neut}$  slightly less exothermic (for weak acid) (1) 3

(iii)  $[H^+]^2 = K_a [CH_3COOH] = 1.74 \times 10^{-5} \times 0.140 = 2.44 \times 10^{-6}$

$$[H^+] = 0.00156 \text{ (mol dm}^{-3}\text{)} \text{ (1)}$$

$$\text{pH} = 2.81 \text{ consequential on } [H^+] \text{ but not } \text{pH} > 7 \text{ (1)}$$

ACCEPT 2.80/2.8 (answers to 1 or 2 dp)

The assumptions are **two** from:

$$[H^+] = [CH_3COO^-] - \text{this mark can be earned from working /}$$

negligible  $[H^+]$  from ionisation of water (1)

$$[CH_3COOH] = 0.140 - [H^+] \approx 0.140 \text{ (mol dm}^{-3}\text{)} / \text{ionisation of acid}$$

negligible (1)

solution at 25°C (1) **max 2**

4

$$(iv) \quad 1.74 \times 10^{-5} = \frac{[H^+][salt]}{[acid]} \text{ (1)}$$

$$[H^+] = 1.74 \times 10^{-5} \times \frac{0.070}{0.100} = 1.22 \times 10^{-5} \text{ (1)}$$

$$\text{pH} = 4.91 / 4.9 / 4.92 \text{ NOT } 5$$

**Max 2** if 0.140 / 0.200 is used (1)

3

[14]

23. (a) (i)  $+313.4 - 4 \times 197.6 - 29.9$  (1) Absence of  $4 \times$  (0)

$$= -506.9 \text{ J mol}^{-1}\text{K}^{-1} \text{ OR } -507 \text{ J mol}^{-1}\text{K}^{-1} \text{ OR answer in kJ (1)}$$

NOT - 510 ie 2 SF

Missing or wrong units ie answer does not match units **1 max**

2

(ii) Negative as expected because only 1 mole of gas on the RHS but 4 moles of gas on the LHS

Mark can be awarded if answer based on moles only rather than states [5 moles  $\rightarrow$  1 mole]

1

$$(iii) \quad \Delta S^\ominus_{\text{surroundings}} = -\Delta H/T \text{ (1) For equation or use of equation}$$

$$= 191\,000 / 323$$

$$= (+) 591 \text{ J mol}^{-1}\text{K}^{-1} \text{ (1) OR answer in kJ}$$

2

$$\text{ALLOW } (+) 591.3 \text{ J mol}^{-1} \text{ K}^{-1} / (+) 590 \text{ J mol}^{-1} \text{ K}^{-1}$$

ALLOW 2, 3 or 4 SF

+ sign not needed provided there is evidence in calculation to show positive

In (i) and (ii) missing units is penalised once UNLESS a different unit error is made – hence penalise twice)

(iv)  $\Delta S^\ominus_{\text{total}}$  is positive/(+84  $\text{J mol}^{-1}\text{K}^{-1}$ ) so reaction should go forwards  
ALLOW TE from (a)(i)

1

(b) (i)  $K_p = \frac{p_{Ni(CO)_4}}{p_{CO}^4}$  if square brackets [ ] are used (0)

1

- (ii) Ni(CO)<sub>4</sub> moles at eq 0.25 (1)  
total number of moles = 99.25

$$P_{\text{Ni(CO)}_4} = \frac{0.25}{99.25} \times 1 = (0.00252) \quad P_{\text{CO}} = \frac{99}{99.25} = (0.9975) \quad (1)$$

*2<sup>nd</sup> mark must be to at least 3 SF or working must be shown ie some evidence that ÷ their total number of moles*

$$K_p = 0.25 / 99.25 / (99/99.25)^4 \\ = 2.54 \times 10^{-3} \quad (1) \text{ atm}^{-3} \quad (1)$$

*Units marked independently*

*ALLOW 2.5 × 10<sup>-3</sup>*

*Many have total number of moles as 100 even when it is not – ALLOW TE for 2<sup>nd</sup> and 3<sup>rd</sup> mark if it should be 100 or just TE for third mark if it shouldn't be 100 from their working*

*[K<sub>p</sub> = 2.6 or 2.60 × 10<sup>-3</sup>] 4*

- (iii) Increasing the pressure/ concentration of CO would force the reaction to the RHS with the smallest number of gaseous molecules (1)

*NOT pressure with rate*

Reduce the temperature so that the reaction goes in the exothermic direction / increase the temperature to increase rate (1)

Do not allow equilibrium to be reached by passing the CO over the nickel/recovering the product formed (1)

Use a catalyst to increase rate / increase the surface area of the nickel to increase number of collisions (1)

3

- (c) The reaction can be reversed by increasing the temperature (1)

as  $\Delta S_{\text{surroundings}}^{\ominus}$  will become less positive/more negative as the temperature is increased (and  $\Delta S_{\text{system}}$  will remain almost unchanged) so  $\Delta S_{\text{total}}$  becomes negative for the forward reaction (1)

2

[16]

24. (a) starts at 2.2 (1)  
vertical section at 40cm<sup>3</sup> of sodium hydroxide (1)  
vertical section centred between pH 8-9 and between 2 to 3 squares high (1)  
shape to include initial jump and finish between pH = 12 – 13 (1)  
If curve drawn back to front, only 2<sup>nd</sup> and 3<sup>rd</sup> marks available

4

- (b) (i) maintains **nearly** constant pH / resists change in pH (1)  
on adding **small amounts** of acid or alkali (1) 2

(ii) 
$$[H^+] = \frac{K_a[acid]}{[salt]} \quad OR \quad pH = pK_a - \lg \frac{[acid]}{[salt]} \quad (1)$$

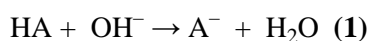
$$[H^+] = 1.78 \times 10^{-4} \times \frac{0.25}{0.125} \quad (1)$$

$$[H^+] = 3.56 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \quad 3$$

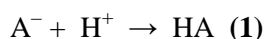
$$pH = 3.4(5) \quad (1)$$

*IGNORE no. of decimal places but penalise pH = 3*

- (iii) acid partially ionised and salt fully ionised  
*OR* equations (1)



*ALLOW*  $H^+ + OH^- \rightarrow H_2O$  followed by more dissociation of HA



[HA] **and** [A<sup>-</sup>] are large (relative to H<sup>+</sup> and OH<sup>-</sup> added) / large reserves of undissociated acid **and** salt (and so the values of [HA] and [A<sup>-</sup>] do not change significantly) (1)

NOTE: If no equations given for effect of adding OH<sup>-</sup> and H<sup>+</sup>, correct explanation can score (1) out of these two marks. 4

[13]

25. (a) (i) Negative with some sensible explanation eg fewer moles of product (1)  
3 moles of gases going to 2 moles of gases (1) 2  
*MUST mention gases or no changes in state*

- (ii) Positive *with some explanation* eg exothermic so surroundings gain entropy (1)

$$\Delta S_{\text{surroundings}} = - \frac{\Delta H}{T} \quad [OR \text{ given in words}]$$

*OR*

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad [OR \text{ given in words}]$$

as reaction goes,  $\Delta S_{\text{total}}$  must be positive therefore  $\Delta S_{\text{surroundings}}$  must be positive

*OR*

Surroundings gain energy so more ways of arranging energy (1) 2



(b) (i) 
$$(K_p) = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} \quad (1)$$

Check that it is **not** a “+” on denominator.

ALLOW ( ) but NOT [ ] eg ALLOW  $((P_{\text{NO}_2})^2)^2$  etc

ALLOW  $(p\text{NO}_2)^2$

$\text{Atm}^{-1} / \text{Pa}^{-1} / \text{kPa}^{-1} / \text{m}^2 \text{N}^{-1} \quad (1) - 2^{\text{nd}} \text{ mark dependent on } 1^{\text{st}}$

ALLOW  $\text{atms}^{-1} / \text{atmospheres}^{-1}$

NOT  $\text{atm}^-$  etc

NOT  $\text{Kpa}^{-1}$

2

(ii) Temperature

A lower temperature is needed to get a better yield (and would cost less) because the reaction is exothermic (1)

but the lower temperature may slow the reaction down too much

OR reverse argument (1)

Pressure

A high pressure will increase yield as only two moles on the right compared to three on the left/less moles on the right hand side (1)

It will also increase the rate of the reaction (1)

Low pressure because of cost only gets mark if higher yield at higher pressure identified

To award any of the yield marks must say why

4

(c) (i) Must be a quantity that can be measured

Eg

The pressure could be measured (1)

as it will decrease as the reaction proceeds because there are only two/fewer moles on the right compared to three on the left (1)

OR colour (1)

as the nitrogen(IV) oxide is brown whereas the other gases are colourless (1)

OR total volume (1)

which will decrease by one third/because there are fewer moles (1)

ALLOW acidity because  $\text{NO}_2$  acidic **and** others not (1 max)

NOT dilatometry

NOT temperature

2

(ii)  $[\text{NO}]$  second order (1)

because when conc of NO is doubled, the rate goes up four times (1)

$[\text{O}_2]$  first order (1)

3

Then (iii), (iv) and (v) must follow consistently from (ii)

(iii) ALLOW TE from (ii) e.g.

rate = $k[\text{NO}]^2[\text{O}_2]$	rate = $k[\text{NO}][\text{O}_2]$	1
-------------------------------------	-----------------------------------	---

(iv) third / 3	second / 2	1
----------------	------------	---

(v) 8000 (1) $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$ (1)	8 (1) $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (1)	
<i>Units can be given in any order</i>		2

(d) The activation energy must be low <i>OR</i> bond energies low <i>NOT</i> “more successful collisions” <i>NOT</i> large rate constant		1
---	--	---

**[20]**

26.	(a)	(i)	- lg (0.05) = 1.3(0)		1
<i>IGNORE sig figs from this point on in this question</i>					

(ii)	[OH <sup>-</sup> ] = $1 \times 10^{-14} / 0.05 = 2 \times 10^{-13}$ (mol dm <sup>-3</sup> )		1
<i>OR via pOH</i>			
<i>Correct answer with no working (1)</i>			

(b)	(i)	$K_a = [\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]/[\text{H}_3\text{PO}_4]$ <i>NOT</i> using H <sup>+</sup> instead of H <sub>3</sub> O <sup>+</sup>		1
-----	-----	---	--	---

(ii)	$[\text{H}_3\text{O}^+] = 10^{-1.20}$ $= 0.063$ (mol dm <sup>-3</sup> ) (1)		
------	--	--	--

$K_a = \frac{0.063^2}{0.500 - 0.063}$ (1)	<i>NOT consequential on (b)(i)</i>
---	------------------------------------

$= 9.08 \times 10^{-3}$ (1) mol dm <sup>-3</sup> (1)	
$= 9.11 \times 10^{-3}$ if [H <sub>3</sub> O <sup>+</sup> ] not rounded	

*ALLOW*

$K_a = \frac{0.063^2}{0.500}$ (1)	
$= 7.94 \times 10^{-3}$ (1) mol dm <sup>-3</sup> (1)	
$= 7.96 \times 10^{-3}$ if [H <sub>3</sub> O <sup>+</sup> ] not rounded	4

*ALLOW consequential marking on numerical errors*

*Correct answer with units and some working (4)*

(c)	(i)	Assign the terms ‘acid/base’ (1) link the pairs (1)		2
-----	-----	--	--	---

(ii) presence of  $H^+$  from the first dissociation keeps equilibrium to left /suppresses ionisation 1

(d) Bromocresol green (1)

$pK_{in}$ /range/colour change (of indicator) lies in vertical section

OR

For alternative indicators  $pK_{in}$ /range/colour change (of indicator) lie outside vertical section (1) 2

[12]

27. (a) pentyl dichloroethanoate (1)  
*ALLOW* 1,1 OR 2,2-  
*ALLOW* pent-1-yl /*all one word*  
*NOT* penten  
*NOT* pentan  
*NOT* pentanyl

ester (1)

*ALLOW* esther 2

(b) (i) using a pipette remove a known volume (say  $20\text{ cm}^3$ ) (1)

remove some solution – either with a pipette

*OR* a known volume /  $20\text{ cm}^3$

titrate with an alkali (such as sodium hydroxide) (1)

of known concentration (1)

– *dependent on previous mark ie must have mentioned alkali*

*IGNORE* quenching

using a named indicator eg. phenolphthalein/methyl orange (1)

*NOT* litmus / universal indicator

Measure pH on its own 1 (out of 4)

*But if calculation fully explained from pH can get full marks* 4

(ii) 
$$K_c = \frac{[CHCl_2COOC_5H_{11}(l)]}{[CHCl_2COOH(l)] \times [C_5H_{10}(l)]}$$

*State symbols not required* 1

(iii)  $C_5H_{10}$                       1.7 (1)  $\frac{1.7}{0.3} = 5.67(5.7)$  NOT 5.66  
 $CHCl_2COOC_5H_{11}$             0.6 (1)  $\frac{0.6}{0.3} = 2$

(1) for  $\div$  moles at eq by 0.3 in both cases 3

(iv)  $2K_c = \frac{0.6/0.3}{1.33} \times 1.7 / 0.3$  (1)  $= \frac{2}{1.33 \times 5.67}$   
 $= 0.265$  (1)  $dm^3 mol^{-1} / mol^{-1} dm^3$  (1)

NOT  $dm^{-3}$

ALLOW 0.27 / 0.26 / 0.264

Penalise 1 SF or 4SF or more SF but only take off 1 mark maximum in (iii) and (iv) for significant figure errors

ALLOW TE from expression in (ii)

TE using numbers for (iii) full marks possible 3

[13]

28. (a) Enthalpy/heat/energy change for **one mole** of a compound/substance/ a product (1)

**NOT** solid/molecule/species/element

*Reject "heat released or heat required" unless both mentioned*

to be formed from its **elements** in their **standard** states (1)

ALLOW normal physical state if linked to standard conditions

*Reject "natural state" / "most stable state"*

standard conditions of 1 atm pressure and a stated temperature (298 K) (1) 3

*Reject "room temperature and pressure"*

*Reject "under standard conditions"*

(b) (i) Bonds broken                      Bonds made  
 $\text{N}\equiv\text{N}$  (+)945                       $6\text{N}-\text{H}$  (-)2346 (1)  
 and

$3\text{H}-\text{H}$  (+)1308 (1)  
 (+)2253

$\Delta H = 945 + 1308 - 2346$   
 $= -93$  sign and value (1)

$\Delta H^\ominus = -93 = -46.5$  ( $\text{kJ mol}^{-1}$ )  
 sign and value q on 3<sup>rd</sup> mark (1)

2

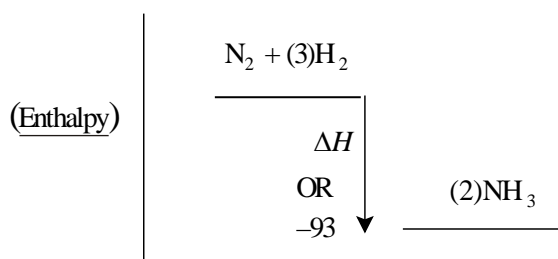
4

*Accept  $-46.5$  ( $\text{kJ mol}^{-1}$ ) with working (4)*

*Accept  $+46.5$  with working **max** (3)*

*Accept  $+93$  with working **max** (2)*

(ii)



*Accept  $-46.5$*

Correct labelled levels (1)

*Reject "Reactants" and "Products" as labels*

$\Delta H$  labelled (1)

direction of arrow must agree with thermicity

*Accept double headed arrow*

*Diagram marks cq on sign and value of  $\Delta H$  in (b)(i)*

*IGNORE activation energy humps*

2

(iii) 350–500 °C (1)

*Accept any temperature or range within this range*

higher temperature gives higher rate (1)

but a lower yield because reaction is exothermic (1)

*Accept favours endothermic reaction **more than** exothermic so lower yield*

OR

Lower temperature give higher yield because reaction is exothermic (1)

but rate is slower (1)

3

*Accept cq on sign of  $\Delta H_f$  in (b)(i) or levels in (ii)*

*Reject lower temp favours exothermic reaction*

- (iv) Iron / Fe (1) IGNORE any promoters  
no effect on yield (1) 2
- (v) temp would have to be much higher for a reasonable rate then  
yield would be too low  
“lower activation energy” implies reasonable rate  
OR  
Allows reaction at a lower temp at a reasonable/fast rate giving  
a reasonable yield. 1
- Accept rate too slow without catalyst at a temp giving a  
reasonable yield*
- Reject to lower activation energy of reaction*
- (c) (i) advantage  
higher (equilibrium) yield/more NH<sub>3</sub> in equilibrium  
mixture/equilibrium shifts to right (1)
- because smaller number of (gaseous) moles/molecules on rhs (1)  
*IGNORE any reference to change in rate* 2
- Reject just “more ammonia”*
- (ii) disadvantage  
(plant more) expensive because thicker pipes would be needed
- OR  
cost (of energy) for compressing the gases/cost of pump  
OR  
Cost of equipment/pressure not justified by higher yield 1
- Accept stronger or withstand high pressure for thicker*
- Accept vessel/container/plant /equipment/reaction vessels for  
pipes*
- Reject “just more expensive”*
- Reject “just thicker pipes etc”*
- Reject apparatus*

29. IGNORE s.f. throughout this question

(a) Acid

Proton or  $H^+$  donor

Or forms  $H^+$  or  $H_3O^+$  (1)

Weak

dissociates to a **small** extent

Or ionises to a **small** extent (1)

2

*Accept few molecules dissociate*

*Or incomplete dissociation*

*Or partial dissociation*

*Reject "not fully dissociated"*

*Or "not dissociated fully"*

(b)  $2HCOOH(aq) + Na_2CO_3(aq) \rightarrow 2HCOONa(aq) + CO_2(g) + H_2O(l)$

Or

$HCOOH(aq) + Na_2CO_3(aq) \rightarrow HCOONa(aq) + NaHCO_3(aq)$

Species + balancing (1)

State symbols (1) *Consequential on correct species*

2

*Accept ...  $\rightarrow 2HCOONa(aq) + H_2CO_3(aq)$*

*Accept  $HCO_2H$  for the acid*

*Accept  $HCO_2Na$  or  $HCOO^-Na^+$  for salt*

(c) (i) one acid:  $HCOOH$

Conjugate base:  $HCOO^-$

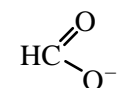
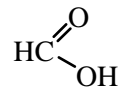
**1 mark for both**

*Accept correct acids and conjugate bases in either order*

*ACCEPT*

*$HCO_2H$  and  $HCO_2^-$*

*OR*



other acid:  $H_3O^+$

Conjugate base:  $H_2O$

**1 mark for both**

2

*Reject  $H^+$  for  $H_3O^+$*

$$(ii) \quad (K_a) = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

*Accept  $[H^+]$  instead of  $[H_3O^+]$*

Must use square brackets

1

*$[HCO_2^-]$  and  $[HCO_2H]$*

$$(iii) \quad [H^+]^2 = K_a \times [HCOOH]$$

OR

$$K_a = \frac{[H^+]^2}{[HCOOH]}$$

OR

$$[H^+]^2 = 1.60 \times 10^{-4} \times 0.100 \quad (1)$$

$$[H^+] = \sqrt{1.60 \times 10^{-4} \times 0.100}$$

$$= 4.0 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} \quad (1)$$

*pH = 4.8 scores (2) as square root has not been taken*

IGNORE sig figs

**Max 1** if  $[H^+]^2$  expression incorrect

$$pH = -\log_{10}[H^+]$$

$$pH = 2.40 \quad (1)$$

*Accept any pH value consequential on  $[H^+]$ , provided  $pH < 7$*

*Reject  $pH = 2.39$  (is a rounding error) so no third mark*

Alternative method

$$pK_a = 3.80 \quad (1)$$

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log[\text{acid}] \quad (1)$$

$$pH = 1.90 - (-0.50)$$

$$pH = 2.40 \quad (1)$$

3

*Reject  $pH = 2.39$  (is a rounding error) so no third mark*



(d) (i)  $[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]}$

OR

$$[H^+] = 1.60 \times 10^{-4} \times \frac{0.0500}{0.200} \quad (1)$$

$$= 4.00 \times 10^{-5} \text{ (mol dm}^{-3}\text{)} \quad (1)$$

$$\text{Reject } \frac{0.100}{0.400}$$

$$\text{pH} = 4.40 \quad (1) \text{ IGNORE sig figs}$$

*Reject 4.39 (rounding error) so no third mark*

OR

$$\text{pH} = \text{p}K_a - \log_{10} \left\{ \frac{[\text{HCOOH}]}{[\text{HCOO}^-]} \right\} \quad (1)$$

$$\text{pH} = -\log_{10}(1.60 \times 10^{-4}) - \log_{10} \left\{ \frac{0.0500}{0.200} \right\} \quad (1)$$

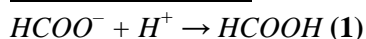
$$\text{Reject } \frac{0.100}{0.400}$$

$$\text{pH} = 3.80 - (-0.60)$$

$$\text{pH} = 4.40 \quad (1) \text{ IGNORE sig figs}$$

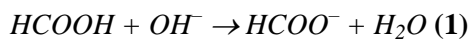
*Reject 4.39 (rounding error) so no third mark*

(ii) Addition of H<sup>+</sup> ions:



Accept if described in terms of  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$  shifting to left

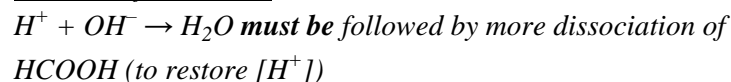
Addition of OH<sup>-</sup> ions:



If the ionisation of sodium methanoate shown with

$\rightleftharpoons$  then **max (1)** out of 2 for above equations

Addition of OH<sup>-</sup> ions:



Accept “molecular” equations or equations described in words or notation involving HA, H<sup>+</sup> and A<sup>-</sup>.

(buffer solution has) high concentrations

Or a large reservoir of **both HCOOH and HCOO<sup>-</sup>**

relative to added H<sup>+</sup> / OH<sup>-</sup> **(1)**

(hence virtually no change in [H<sup>+</sup>])

3

Accept just “large reservoir of both HCOOH and HCOO<sup>-</sup>”

[16]

30. (a) **IGNORE s.f. throughout this question**

(i) **moles SO<sub>2</sub>** (10.0 – 9.00) = 1.00 (mol)

**moles O<sub>2</sub>** (5.00 – 4.50) = 0.500 (mol)

**moles SO<sub>3</sub>** 9.00 (mol)

all 3 correct → **(2)**

2 correct → **(1)**

2

Reject multiples of the stated moles

(ii) All three ÷ total number of moles **(1)**

i.e.

$$X_{\text{SO}_2} = \frac{1.00}{10.5} (= 0.0952) \text{ or } \frac{2}{21}$$

$$X_{\text{O}_2} = \frac{0.500}{10.5} (= 0.0476) \text{ or } \frac{1}{21}$$

$$X_{\text{SO}_3} = \frac{9.00}{10.5} (= 0.857) \text{ or } \frac{18}{21} \text{ or } \frac{6}{7}$$

Reject rounding to 1 sig fig

Mark consequential on (a)(i)

1

- (iii) All three  $\times$  total pressure (1)  
i.e.

$$p_{\text{SO}_2} = \frac{1.00}{10.5} \times 2.00 \text{ or } \frac{4}{21}$$

$$= 0.190 \text{ (atm)}$$

$$p_{\text{O}_2} = \frac{0.500}{10.5} \times 2.00 \text{ or } \frac{2}{21}$$

$$= 0.0952 \text{ (atm)}$$

$$p_{\text{SO}_3} = \frac{9.00}{10.5} \times 2.00 \text{ or } \frac{36}{21} \text{ or } \frac{12}{7}$$

$$= 1.71 \text{ (atm)}$$

Mark consequential on (a)(ii)

1

(iv)  $K_p = \frac{(1.71)^2}{(0.190)^2 \times (0.0952)}$

$$K_p = 851 \text{ (1) atm}^{-1} \text{ (1)}$$

Mark consequential on (a)(iii) and (a)(iv)

2

*Accept answer with units and no working (2)*

*Accept "correct answers" between 845 and 855 as this covers rounding up etc*

*Reject wrong units e.g. mol<sup>-1</sup> dm<sup>3</sup>*

- (b) (i) ( $K_p$ ) decreases

1

- (ii) ( $K_p$  decreases so)

*Reject any Le Chatelier argument (this prevents access to 1<sup>st</sup> mark)*

fraction/quotient  $\frac{p^2 \text{SO}_3}{p^2 \text{SO}_2 \times p_{\text{O}_2}}$

has to decrease (to equal new  $k_p$ ) (1)

so shifts to **left** hand side (1) – this mark only available if (b)(i) answer was  $k_p$  decreases.

*Reject shifts to right, even if answer to (b)(i) was  $k_p$  increases*

(as  $p_{\text{SO}_3}$  decreases whereas  $p_{\text{SO}_2}$  and  $p_{\text{O}_2}$  increase)

2

- (c) (i) No effect/none/zero (effect)

1

(ii) Increases  
*OR*  
 more SO<sub>3</sub>/more sulphur trioxide  
*OR*  
 increases amount of SO<sub>3</sub>/sulphur trioxide 1

(d) (i) No effect/none/zero (effect) 1  
 (ii) No effect/none/zero (effect) 1

[13]

31. (a) H<sup>+</sup> 1

*Accept H<sub>3</sub>O<sup>+</sup>*

(b) HCOOH/HCO<sub>2</sub>H (1)  
 HNO<sub>3</sub> (1)  
 -1 for each extra incorrect answer 2

*Accept C and E*

[3]

32. (a) (i) pH = 3.5 (1)  
 $\log_{10}[\text{H}^+] = -3.5$   
 $\Rightarrow [\text{H}^+] = 3.16 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} (1)$   
 $2.5(1) \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \text{ based on pH} = 3.6 \text{ (2 marks)}$  2

*Accept T.E. from wrong pH providing < 7*

*Accept  $3.2 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$*

*$3 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$  allowed if evidence of rounding being applied*

(ii)  $K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2^-]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}]} (1)$  1

*Accept version with  $[\text{H}_3\text{O}^+]$*

*Accept molecular formulae*

*Accept  $\frac{[\text{H}^+][\text{C}_4\text{H}_7\text{O}_2^-]}{[\text{C}_4\text{H}_8\text{O}_2]}$*

(iii)  $K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}]} (1)$

$$= \frac{(3.16 \times 10^{-4})^2}{0.00660} \quad (1^{\text{st}} \text{ mark can be scored here})$$

$$= 1.5 \times 10^{-5} \text{ (mol dm}^{-3}\text{) (1)}$$

Ignore units

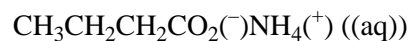
Only 2 sig. fig. allowed

2

*Accept TE from (i)*

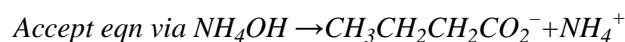
*Allow any number of s.f. provided consistent with calculation*

*Reject TE from (ii)*



Molecular formulae acceptable

1



*Reject any amide product*

(ii) Ammonium butanoate (1)

(Excess) butanoic acid (1)

no TE from (b)(i)

2

*Accept ammonium ions and butanoate ions (1)*

*Reject butanoate ions alone*

*Reject formulae*

(iii) A buffer (mixture) (1)

There is a relatively small **rise /change in pH** (as aqueous ammonia is added) OWTTE (1)

Mark independently

2

*Reject sharp neutralisation point/no change in pH*

(iv) There is no large increase in pH / vertical shape to the graph (at the end-point) OWTTE

1

*Accept no sudden change in pH*

*Reject no indicator has the required pH range*

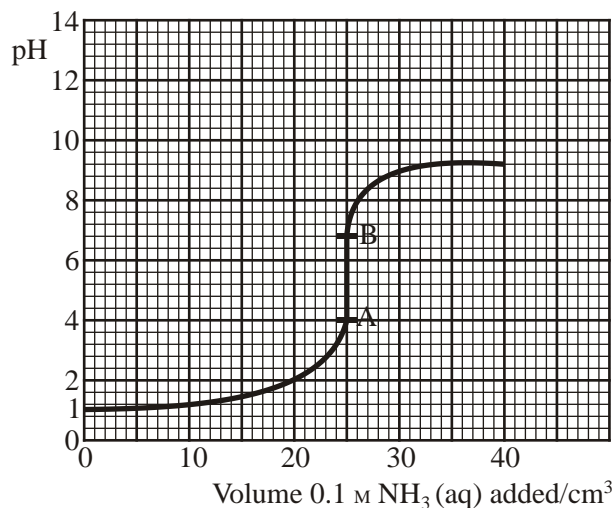
- (v) EITHER  
 End-point = 30 cm<sup>3</sup> (1)  
 $\Rightarrow [\text{NH}_3] = (10/30) \times 0.00660 = 0.00220 \text{ (mol dm}^{-3}\text{)} (1)$   
 OR  
 10 cm<sup>3</sup> of butanoic acid contain  $6.60 \times 10^{-5} \text{ mol}$   
 From equation this requires  $6.60 \times 10^{-5} \text{ mol NH}_3$   
 From graph, end-point = 30 cm<sup>3</sup> (1)  
 $\Rightarrow [\text{NH}_3] = 6.60 \times 10^{-5} \times (1000/30)$   
 $= 2.20 \times 10^{-3} / 0.00220 \text{ (mol dm}^{-3}\text{)}(1)$   
 Allow internal TE for 2<sup>nd</sup> mark based on an incorrect  
 equivalence point i.e. 0.0660 (mol dm<sup>-3</sup>)

2

*Allow T.E. from (b)(i)*

[13]

33. (a)



Do not worry about general shape of the curve, the scoring points are:

- Starting pH ~ 1 **and** finishing pH between 9 and 11 (1)
- Vertical at 25 cm<sup>3</sup> (1)
- Vertical range: at least three pH units in the range 3 to 8  
 e.g. pH range 3 to 6 OR 3 to 7 OR 3 to 8 OR 4 to 7  
 OR 4 to 8 OR 5 to 8 (1)  
 (do not need to start/finish on whole numbers)

*Accept pH range 3 to 5*

- Middle of vertical pH range between 4 and 6 (1)

4

- (b) Bromocresol green  
 Indicator(s) CQ on graph [check table on question paper]

1

*Accept more than one indicator for extended vertical regions*

- (c) pH change around equivalence point too small  
OR pH changes over too big a volume (1)

*Accept too small a vertical (region)*

*OR no vertical (region)*

*OR no point of inflexion*

*OR no sudden change in pH*

*OR no straight section*

for a sharp colour change of indicator (1)

*Accept no sharp/clear/precise end point*

*OR very small range over which indicator changes colour*

*Reject no suitable indicator*

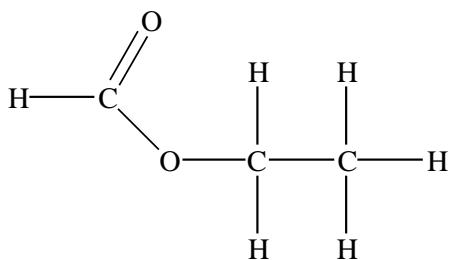
*OR No "easy" colour change*

[If say ammonia is a strong base or ethanoic acid is a strong acid, or both, (0 out of 2)]

2

[7]

34. (a)



1

(b) ester

1

(c) (i) Moles: C<sub>2</sub>H<sub>5</sub>OH: 3.75 (1)

Moles: HCOOC<sub>2</sub>H<sub>5</sub> : 2.50 and moles H<sub>2</sub>O : 2.50 (1) for both

2

(ii) 
$$K_c = \frac{[\text{HCOOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{HCOOH}][\text{C}_2\text{H}_5\text{OH}]}$$

1

*Reject obviously round brackets "( )"*

$$(iii) \quad K_c = \frac{2.50/0.485 \times 2.50/0.485}{0.50/0.485 \times 3.75/0.485} \quad (1)$$

Must have clearly divided moles of each component by 0.485 for 1<sup>st</sup> mark e.g.

$$[\text{HCOOC}_2\text{H}_5] = [\text{H}_2\text{O}] = 5.16 \text{ (mol dm}^{-3}\text{)}$$

$$\text{and } [\text{HCOOH}] = 1.03 \text{ (mol dm}^{-3}\text{)}$$

$$\text{and } [\text{C}_2\text{H}_5\text{OH}] = 7.73 \text{ (mol dm}^{-3}\text{)}$$

= 3.33 (1) **stand alone mark**

IGNORE sig.figs.

2

$$\text{Accept } K_c = \frac{(2.50)^2}{0.50 \times 3.75} = 3.33 \text{ only scores (2) if it is stated}$$

that V cancels either here or in (iv)

If  $[\text{H}_2\text{O}]$  omitted in (ii), then answer

$$K_c = 0.647 \text{ mol}^{-1} \text{ dm}^3$$

(2) but this will give

$$K_c = 1.33 \text{ mol}^{-1} \text{ dm}^3 \text{ with V omitted from calculation (1)}$$

Reject 1<sup>st</sup> mark if 485 used as V in expression

(iv) No, (as) equal numbers of moles on both sides

OR volumes cancel

OR mol dm<sup>-3</sup> cancel

OR units cancel

OR crossing out units to show they cancel

1

Accept "equal powers/moles on both sides"

OR "powers cancel"

Mark CQ on  $K_c$  expression in (ii)

Reject "concentrations cancel"

(d) (i) (as reaction) endothermic (1)

Accept exothermic in backward direction (or words to that effect)

$K_c$  decreases (1)

If state exothermic in forward direction, **1 mark only (out of 4)** for CQ "increase in  $K_c$ "

numerator in quotient (has to) decrease

OR denominator in quotient (has to) increase

OR fraction (has to) decrease (1)

yield of  $\text{HCOOC}_2\text{H}_5$  decreases (1)

4



- (ii) no effect as catalysts do not affect (the value of) K  
 OR  
 no effect as catalysts do not affect the position of equilibrium  
 OR  
 no effect as catalysts do not affect the yield  
 OR  
 No effect as catalysts increase the rate of the forward and  
 backward reactions equally/to the same extent  
 OR  
 no effect as catalysts **only** increase the rate  
 OR  
 no effect as catalysts **only** alter the rate  
 “no effect” can be stated or implied  
 IGNORE any references to activation energy 1

*Reject just “catalysts increase rate”*

**[13]**

35. (a) The amount of a **solid** present is immaterial since  $K_c$  does not depend on  
 this  
 OR **solids** do not appear in expression for equilibrium constants  
 IGNORE any references to solid in excess. 1
- (b)  $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}$   
 IGNORE state symbols 1

- (c) Correct answer with some working and correct units scores full marks. Otherwise steps in calculation must make it reasonably clear to examiner what is being calculated (QWC).

$$\text{(initial amount) } \Gamma = 0.100 \text{ mol dm}^{-3} \times 0.050 \text{ dm}^3 = 5 \times 10^{-3} \text{ mol (1)}$$

$$\text{Amount } \text{Ag}^+ = 0.100 \text{ mol dm}^{-3} \times 0.031 \text{ dm}^3 = 3.1 \times 10^{-3} \text{ mol (1)}$$

$$\therefore \text{equilibrium amount } \Gamma = 3.1 \times 10^{-3} \text{ mol (1)}$$

$$\Gamma \text{ reacted} = (5 - 3.1) \times 10^{-3} \text{ mol} = 1.9 \times 10^{-3} \text{ mol (1)}$$

If this subtraction is not carried out then the next mark (for calculating amount of sulphate) can not be awarded.

$$\text{Thus amount of sulphate} = \frac{1}{2} \times 1.9 \times 10^{-3} (= 9.5 \times 10^{-4} \text{ mol}) \text{ (1)}$$

$$\text{conc iodide} = \frac{3.1 \times 10^{-3} \text{ mol}}{0.05 \text{ dm}^3} (= 0.062 \text{ mol dm}^{-3})$$

$$\text{AND conc sulphate} = \frac{0.95 \times 10^{-3} \text{ mol}}{0.05 \text{ dm}^3} (= 0.019 \text{ mol dm}^{-3}) \text{ (1)}$$

The mark is for the process of dividing by  $0.05 \text{ dm}^3$

$$K_c = 0.019/0.062^2 = 4.94 \text{ (1) Answer must be to 2 or more S.F.}$$

Value consequential on dividing their moles by a volume.

$$\text{mol}^{-1} \text{ dm}^3 \text{ (1) Stand alone}$$

8

[10]

36. (a) (i) Pairs: acid  $\text{NH}_4^+$  / ammonium ion and base  $\text{NH}_3$  / ammonia  
acid  $\text{H}_3\text{O}^+$  / hydronium ion and base  $\text{H}_2\text{O}$  / water

1

*Accept hydroxonium ion*

(ii)  $K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$  ignore lower case k

1

$$\text{Accept } K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

*Reject answers including  $[\text{H}_2\text{O}]$*

(iii)  $[\text{H}_3\text{O}^+] = 10^{-5} \text{ mol dm}^{-3}$  (1)

Assumption ionization of  $\text{NH}_4^+$  (negligibly) small (1)

Assumption  $[\text{NH}_3] = [\text{H}_3\text{O}^+]$  (1)

*Accept  $[\text{NH}_4^+] = [\text{NH}_4\text{Cl}]$  or  $\text{NH}_4\text{Cl}$  totally ionized*

thus  $[\text{NH}_4\text{Cl}] = (1 \times 10^{-5})^2 / 5.62 \times 10^{-10}$

$= 0.178 \text{ mol dm}^{-3}$  (1)

Answer to 2 or more S.F.

4

(iv) QWC

methyl red (1)

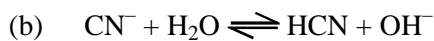
indicator constant or  $\text{p}K_{\text{In}}$  must be near the endpoint pH

OR indicator constant or  $\text{p}K_{\text{In}}$  must be near 5 (1)

2<sup>nd</sup> mark conditional on correct indicator

2

*Accept  $\text{p}K_{\text{In}}$  in the steep part of the graph or it is a weak base-strong acid titration*



IGNORE state symbols

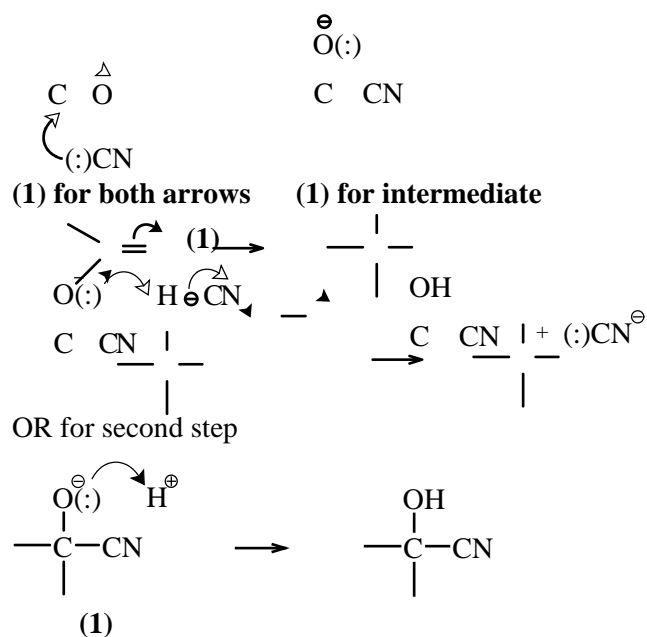
1

*Accept “ $\rightarrow$ ” instead of “ $\rightleftharpoons$ ”*

(c) (i) nucleophilic addition

1

(ii)



3

*Fish hook arrows (penalise once)*

- Ignore the groups attached to the carbonyl carbon throughout
- The intermediate is not consequential on their first step
- The minus of the cyanide ion can be on either the C or the N
- The arrow can start from the minus of  $\text{CN}^-$  in step 1 (but not from the minus of  $\text{CN}^-$ ) and can start from the minus of  $\text{O}^-$  in step 2
- The arrow from the bond must not go past the O atom
- Lone pairs not essential
- Single step addition of HCN or initial attack by  $\text{H}^+/\text{HCN}$  scores zero
- Autoionisation of  $\text{C}=\text{O}$  can only score the last two marks ie max 2

(iii) QWC

if too acidic too small a concentration of cyanide ions **(1)**

*Accept not enough / too little  $\text{CN}^-$*

if too alkaline too little HCN to donate the proton in the last step

OR  $\text{H}^+$  ion concentration too low **(1)**

2



Must be an equation

Must be [ ] NOT ( )

Ignore upper case K

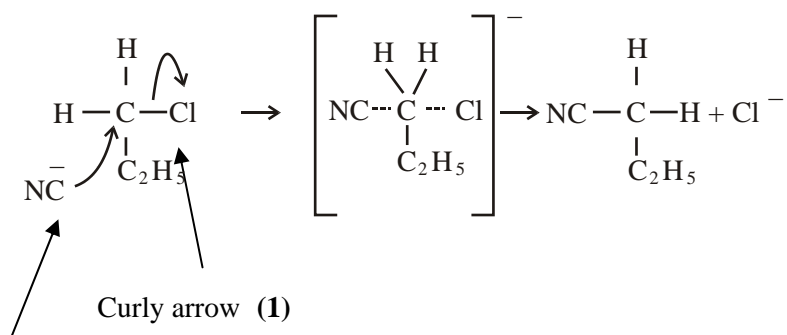
1

Accept 'R' or 'r' for rate  $\text{C}_3\text{H}_7\text{Cl}$  / [1-chloropropane] /  
[chloropropane]

Accept [cyanide ion]/[cyanide]

Reject [KCN]

(ii)



Curly arrow (1)

Transition state (1)

- Must have partial bonds in transition state
- CN and Cl must be on opposite sides of central C in the transition state
- Accept negative charge on N of cyanide ion

3

Mechanism based on  $S_N2$  scores 0

Reject fish hook arrows (penalise once)

Reject arrow from N of CN

[19]

37. (a) (i)  $[6 \times 188.7 + 4 \times 210.7] - [4 \times 192.3 + 5 \times 205]$  (1)

$+180.8 \text{ J mol}^{-1} \text{ K}^{-1}$  (1)

Accept  $+181 \text{ J mol}^{-1} \text{ K}^{-1}$

Reject internal TE

-1 for missing + sign/missing or incorrect units but penalise only once in part (a)

[IGNORE sig fig]

2

- (ii) yes, as **9 molecules of gas** are being changed to **10 molecules of gas** (therefore increase in disorder) 1  
*Accept TE from (i)*  
*Not just 9 molecules going to 10 molecules*
- (iii)  $-905.6 \times 1000 / 1123$  **(1)**  
 $+ 806.4 \text{ J mol}^{-1} \text{ K}^{-1} / 0.8064 \text{ kJ mol}^{-1} \text{ K}^{-1}$  **(1)**  
 [IGNORE SF] 2  
*Accept + 806 J mol K<sup>-1</sup>*
- (iv)  $+987.2 \text{ J mol}^{-1} \text{ K}^{-1}$  1  
*Accept +987 J mol<sup>-1</sup> K<sup>-1</sup>*  
*allow TE from (i) & (iii)*  
*No TE if J mol<sup>-1</sup> K<sup>-1</sup> added to kJ mol<sup>-1</sup> K<sup>-1</sup>*
- (v) All products/reaction goes to completion because  $\Delta S_{\text{tot}} > 200 \text{ J mol}^{-1} \text{ K}^{-1} / \Delta S_{\text{tot}}$  is **very** large 1  
 [Needs to be consistent with (iv)]
- (vi) catalysed pathway should have lower  $E_a$  than uncatalysed pathway and the peak of the curve should be above the energy level of the reactants **(1)**  
 Energy of products should be lower than energy of reactants **(1)** 2
- (b) (i)  $K_p = \frac{p\text{NO}_2^2}{p\text{NO}^2 \times p\text{O}_2}$  1  
*Accept  $\frac{p^2 \text{NO}_2}{p^2 \text{NO} \times p\text{O}_2}$*   
*Reject [ ]*

(ii) mole fraction  $\text{NO}_2 = \frac{4.95}{5}$  or 0.99 (1)

mole fraction  $\text{NO} = \frac{0.025}{5}$  or 0.005

OR

mole fraction  $\text{O}_2 = \frac{0.025}{5}$  or 0.005 (1)

$$K_p = \frac{(0.99)^2 (1.5)^2}{(0.005)^3 (1.15)^3} = 5227200 / 5.2 \times 10^6 \text{ (1)}$$

$\text{atm}^{-1}$  (1) unit mark independent but consistent with expression used in calculation.

IGNORE SF

4

*Correct answer for  $K_p$  alone = 3 max*

- (iii) Equilibrium lies to RHS/products side as  $K_p$  is large  
OR reaction won't go to completion as  $K_p < 10^{10}$   
Must be consistent with (ii)

1

*Allow TE from b(ii)*

- (iv)  $K_p$  remains unchanged as pressure does not affect it / only temperature affects  $K_p$  (1)

partial pressure of  $\text{NO}_2$  increases as eqm moves to side of fewest (gas) molecules/RHS (1)

or

Partial pressure of  $\text{NO}_2$  increases as  $pp = \text{mole fraction} \times \text{total pressure}$

2

*Accept justification in terms of entropy*

[17]

38. (a) (i)  $K_a = \frac{[\text{CH}_2\text{ClCO}_2^-][\text{H}^+]}{[\text{CH}_2\text{ClCO}_2\text{H}]}$

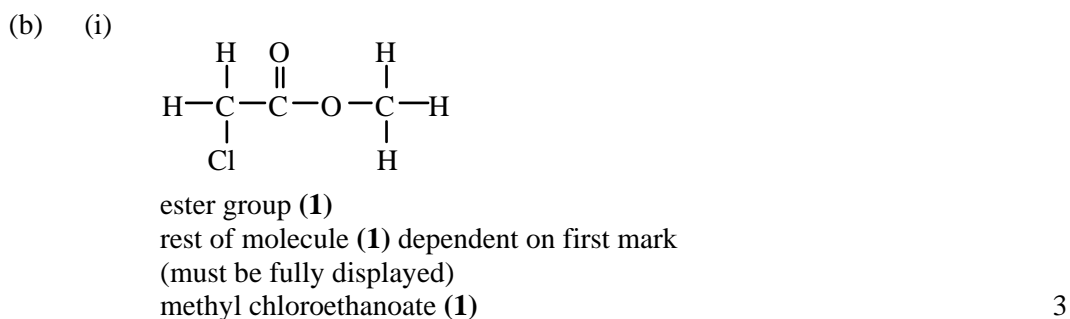
1

*Accept  $[\text{H}_3\text{O}^+]$  in place of  $[\text{H}^+]$*

*allow one set of sq brackets to be missing*

(ii)  $[H^+]^2 = 1.3 \times 10^{-3} \times 0.001$  (1)  
 $= 1.3 \times 10^{-6}$   
 $[H^+] = \sqrt{1.3 \times 10^{-6}}$   
 $1.14 \times 10^{-3}$  (1)  
 $pH = -\log 1.14 \times 10^{-3} = 2.9(4)$  (1)  
 [IGNORE SF] 3

(iii) Trichloroethanoic, as it has the largest  $K_a$  value (1)  
 and has (3 electron withdrawing) chlorine atoms to stabilise  
 the anion formed (on dissociation). (1) 2



*No transferred error for name*

(ii) ester(s) 1  
*Reject ether*

(iii) nucleophile, (1)  
 as it has a lone pair (of electrons) on the (hydroxyl) oxygen (1)  
 which can attack the **positive carbonyl carbon** on the acid (1) 3  
*2<sup>nd</sup> and 3<sup>rd</sup> marks could be obtained by use of a diagram*  
*Reject attack by  $CH_3O^-$*

(iv) (reflux) heat with NaOH(aq) (1)  
 (cool) and add HCl(aq) (1)  
 OR  
 reflux (1) [must be in context]  
 with HCl (1) 2



39. (a) N/N<sub>2</sub> goes from 0 to -3 = reduction (1)  
 H/H<sub>2</sub> goes from 0 to (+)1 = oxidation (1) 2
- If “the oxidation number of N goes down hence reduced and the oxidation number of H goes up and hence oxidised” (max 1)*
- If all O.N. correct but fails to state which is oxidation and which is reduction scores 1.*
- If all O.N. correct but both reactions misclassified, scores zero. Any answer not referring to nitrogen or hydrogen scores zero.*
- (b) (i) Calculation of bonds broken  $463 \times 3 + 944/ (= 2252)$  (1)  
 Calculation of bonds made  $388 \times 6/ (= 2328)$  (1)  
 $\Delta H = -76$  (kJ mol<sup>-1</sup>) (1)  
 mark consequential on numerical values calculated above 3
- Correct answer with some working scores 3 marks*
- Correct answer alone scores 2 marks*
- (ii) Average / mean bond enthalpy used for **N–H bond / ammonia** 1
- Reject just “average bond enthalpies used”*
- (iii) Thermodynamic:  
 energy level of products lower than that of reactants  
 OR  
 energy released in bond formation > energy used to break bonds (1)  
*Accept  $\Delta H$  negative / reaction exothermic*
- kinetic:  
**high** activation energy (1)  
 because strong N≡N (1)  
 [confusion between thermodynamic and kinetic loses first 2 marks]. 3
- Accept because N≡N is 944/ total bond breaking energy is high/2252(kJ mol<sup>-1</sup>)*

- (c) (i) **QWC**  
One way  
temperature increase therefore molecules have greater (average kinetic) energy **(1)**

*Accept moving faster*

more molecules/collisions have  $E \geq E_{\text{act}}$  **(1)**

Therefore a greater **proportion** of/ more **of the** collisions are successful **(1)**

Ignore greater frequency of collision

*Accept  $E > E_{\text{act}}$  particles for molecules*

*greater frequency of successful collisions/ more successful conditions per unit time*

*Reject just "more successful collisions"*

Another way

addition of (iron) catalyst **(1)**

*Accept platinum catalyst*

*Reject incorrect catalyst*

provides alternative route of lower activation energy **(1)**

EITHER:

A greater proportion of /more of the molecules/collisions have  $E \geq E_{\text{cat}}$ /  
a greater proportion of collisions are successful

*Reject just "more successful collisions"*

OR provides (active) sites (where reactant molecules can bond / be adsorbed) **(1)**

Ignore any answers referring to pressure or concentration.  
Do not penalise just "more collisions are successful" more than once

6

- (ii) **QWC**  
Decrease temperature **(1)**  
because (forward) reaction exothermic **(1)**  
increase pressure **(1)**  
because more moles (of gas) on left **(1)**

4

*Accept low temperature  $\Delta H$  is negative*

*Answer based on endothermic reaction scores 0*

*Accept high pressure*

*Accept molecules for moles*

[19]

40. (a) (i) To slow down the reaction/to stop the reaction  
 OR to quench the reaction  
 OR to freeze the (position of) equilibrium *OWTTE* (1)  
 so that the (equilibrium) concentrations/amounts do not change (1) 2

*Accept to stop equilibrium shifting to the left*

(ii) **First mark:**

$$[H_{2(g)}] = [I_{2(g)}]$$

OR

$$\text{Use of } (5.0 \times 10^{-4})^2 \text{ (1)}$$

*If [HI] not squared, first mark only.*

**Second mark:**

$$[HI_{(g)}]^2 = \frac{(5.0 \times 10^{-4})^2}{0.019}$$

OR

$$0.019 = \frac{(5.0 \times 10^{-4})^2}{[HI_{(g)}]^2}$$

OR

$$[HI(g)] = \sqrt{\left( \frac{(5.0 \times 10^{-4})^2}{0.019} \right)} \text{ (1)}$$

**Third mark:**

$$[HI_{(g)}] = 3.6 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} \text{ (1)}$$

Correct answer scores 3 marks.

Ignore state symbols.

Ignore units unless wrong.

Ignore s.f. 3

*If first mark not awarded, total (0)*

- (b) (i)  $K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$   
 Ignore position of any ( ) 1

*[ ] scores (0)*

(ii) *Each step of this calculation must be looked at.*

1<sup>st</sup> mark is for calculating equilibrium moles

$$H_2 = 0.2$$

$$I_2 = 0.2$$

$$HI = 1.6 \text{ (1)}$$

*Mark consequentially*

2<sup>nd</sup> mark is for dividing these by 2 (to get mole fractions)

$$x_{H_2} = \frac{0.2}{2.0} = 0.1$$

$$x_{I_2} = \frac{0.2}{2.0} = 0.1$$

$$x_{HI} = \frac{1.6}{2.0} = 0.8 \text{ (1)}$$

*Mark consequentially*

3<sup>rd</sup> mark is for multiplying by 1.1 (to get partial pressures)

$$P_{H_2} = \frac{0.2}{2.0} \times 1.1$$

$$= 0.11 \text{ (atm)}$$

$$P_{I_2} = \frac{0.2}{2.0} \times 1.1$$

$$= 0.11 \text{ (atm)}$$

$$P_{HI} = \frac{1.6}{2.0} \times 1.1$$

$$= 0.88 \text{ (atm) (1)}$$

*Mark consequentially*

4<sup>th</sup> mark is for substituting into their expression and calculating  $K_p$

$$K_p = \frac{(0.88)^2}{(0.11) \times (0.11)}$$

$$= 64 \text{ (1)}$$

*Ignore s.f.*

*Correct answer with no working scores (1)*

4

*If moles HI given as 0.8,  $K_p = 16$  max (3)*

- (iii) Same number of moles on each side  
 OR  
 (Total) pressure cancels  
 OR  
 (Pressure) units cancel  
 (May be shown by crossing out etc. in b(ii)) 1

*Accept 'Powers cancel'*  
 OR  
*'They cancel'*  
 OR  
*'Same number of molecules on each side'*  
 Reject **'Partial pressures cancel'**  
 OR  
*'mol dm<sup>-3</sup> cancel'*

[11]

41. (a) (i) One acid: CH<sub>3</sub>CH<sub>2</sub>COOH(aq)  
 Conjugate base: CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup>(aq) (1)  
 Other acid: H<sub>3</sub>O<sup>+</sup>(aq)  
 Conjugate base: H<sub>2</sub>O(l) (1)  
 Ignore state symbols 2

*Accept correct acids with conjugate bases in either order*

- (ii) WEAK: dissociates/ionises to a small extent (1) OWTTE

*Accept 'Few molecules dissociate'*  
*Accept 'Incomplete' or 'partial' dissociation*  
*Accept "Does not fully dissociate"*  
 Reject "ions partially dissociate"

- ACID: proton donor (1) 2

*Accept Produces H<sub>3</sub>O<sup>+</sup> / hydrogen / H<sup>+</sup> ions*

*Reject just "contains H<sub>3</sub>O<sup>+</sup> ...."*

- (b) (i) 
$$K_a = \frac{[CH_3CH_2COO^-][H_3O^+]}{[CH_3CH_2COOH]}$$
 1

*Accept [H<sup>+</sup>] instead of [H<sub>3</sub>O<sup>+</sup>]*

*Reject any expression containing [H<sub>2</sub>O]*

(ii)  $([H^+] =) 3.63 \times 10^{-4} \text{ (mol dm}^{-3}\text{) (1)}$   
Or  $10^{-3.44}$

*If  $K_a$  expression incorrect in (b)(i) or  $[H^+]$  not squared, only 1<sup>st</sup> mark available*

$$[CH_3CH_2COOH] = \frac{[H^+]^2}{1.30 \times 10^{-5}}$$

Or

$$[CH_3CH_2COOH] = \frac{(3.63 \times 10^{-4})^2}{1.30 \times 10^{-5}} \text{ (1)}$$
$$= 0.010 \text{ (1) (mol dm}^{-3}\text{) (1)}$$

ASSUMPTIONS:

**First assumption mark:**

negligible  $[H^+]$  from ionisation of water Or  $[CH_3CH_2COO^-] = [H^+]$  (1)

*Accept "No other source of  $H^+$  ions"*

*Reject **Just** " $CH_3CH_2COO^- = H^+$ " (ie no square brackets)*

**Second assumption mark:**

Ionisation of the (weak) acid is negligible

Or  $x - [H^+] \approx x$  where x is initial concentration of  $CH_3CH_2COOH$

Or  $[H^+] \ll [HA]$  (1)

5

*Accept "**Very** slight ionisation ..."*

*"the initial  $[HA]$  = equilibrium  $[HA]$ "*

*Reject any mention of non-standard conditions or 'temperature not at 298 K'*

- (c) (i) Ignore "A solution of known pH which...."  
maintains **nearly** constant pH  
OR  
resists change in pH (1) OWTTE  
on adding **small amounts** of acid or alkali (1)

Mark independently

2

(ii) Working MUST be checked

**First mark:**

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{base}]} \quad (1)$$

$$\text{Accept } K_a = \frac{[H^+] \times [\text{salt}]}{[\text{acid}]}$$

**Second mark:**

Correct [acid] = 0.0025 and [salt] = 0.00375 (1)

**Third mark:**

Calculation of pH correct consequential on [acid] and [salt] used.

$$[H^+] = 1.30 \times 10^{-5} \times \frac{0.0025}{0.00375}$$

$$= 8.67 \times 10^{-6} \text{ (mol dm}^{-3}\text{)}$$

$$\text{pH} = 5.06 \quad (1)$$

*Accept if [salt] and [acid] inverted, pH is 4.71 (2 marks)*

*Accept inverted with the original concentrations, pH = 5.19 (1 mark)*

Ignore sig fig

OR

**First mark:**

$$\text{pH} = \text{p}K_a - \log_{10} \frac{[\text{acid}]}{[\text{salt}]} \quad (1)$$

*Reject in both cases, if [acid] = [0.0100] and [salt] = [0.00500], pH = 4.59 (2 marks)*

**Second mark:**

Correct [acid] = 0.0025 and [salt] = 0.00375 (1)

**Third mark:**

Calculation of pH correct consequential on [acid] and [salt] used.

$$\text{pH} = 4.89 - \log_{10} \frac{[0.0025]}{[0.00375]} \quad (1)$$

$$= 4.89 - (-0.18)$$

$$= 5.07 \quad (1)$$

*Accept 5.06*

Ignore sig fig

3

[15]

42. (a) (i) 
$$K_p = \frac{(P_{NO})^2}{P_{N_2} \times P_{O_2}}$$

Allow answer with brackets and/or “x” omitted  
Ignore (g) and eq

1

*Accept* 
$$K_p = \frac{P^2_{NO}}{P_{N_2} \times P_{O_2}}$$

*Reject anything in [ ]*

(ii) Same number of moles on each side of the equation OR  
The (partial pressure) units all cancel out (in the expression for  $K_p$ )

1

(b) (i) 
$$(p_{NO})^2 = 0.87 \times 0.23 \times 5.0 \times 10^{-31} \text{ (1)}$$
  
$$= 1.0 \times 10^{-31}$$

$$p_{NO} = \sqrt{(1.0 \times 10^{-31})}$$
  
$$= 3.2 \times 10^{-16} \text{ (atm) (1)}$$

*Accept* 
$$3.16 \times 10^{-16} \text{ (atm) (1)}$$

Ignore sig fig

Mark consequentially only if based on reciprocal of  
correct expression in (a)(i)

2

(ii) 
$$0.87 + 0.23 (+ 3.2 \times 10^{-16}) = 1.10 / 1.1 \text{ (atm)}$$

Allow TE from (b)(i)

1

*Reject answer based on adding  $2 \times p_{NO}$*

(iii) 
$$p_{NO} \text{ doubles/will become } 6.4 \times 10^{-16} \text{ atm (1)}$$

$$K_p \text{ remains constant/is (still) } 5.0 \times 10^{-31} \text{ (1)}$$

Ignore any “neutral” qualifications to these answers

2

*Accept*  $p_{NO}$  will increase

*Reject more than double*

*Reject answers with incorrect reasoning*



- (c) (i) Reaction will occur, but (very) **little**  
 NO is formed  
 OR  
 the equilibrium mixture is mainly  
 (unreacted) N<sub>2</sub> and O<sub>2</sub> 1
- Accept reaction occurs, but equilibrium lies (very much) to the left*
- Reject "Reaction is more likely to occur from right to left" OR "Reverse reaction is favoured", unless included with acceptable answer*
- (ii) No change of state of any of the components is involved  
 (as the gases are heated up) OWTTE  
 OR  
 All components are gases (at these temperatures)  
 IGNORE Any reference to the number of particles involved 1
- (iii) ( $\Delta H$  is positive so)  $-\frac{\Delta H}{T} = \Delta S_{\text{surroundings}}$  will be negative  
 No mark for "negative" alone 1
- Accept negative, since for an endothermic reaction energy is taken from the surroundings causing a decrease in disorder / reduction in entropy*
- (iv) (As T increases)  $\Delta S_{\text{surroundings}}$  becomes greater/less negative/  
 more positive, so  $\Delta S_{\text{total}}$  (also) becomes greater/less  
 negative/more positive/increases 1
- Accept  $\Delta S_{\text{surroundings}}$  becomes "smaller", if qualified, e.g. becomes closer to zero*
- (d) Equilibrium might not have been reached (in the very short time the  
 gases are present in the engine)  
 Ignore references to the fact that the system is not "closed" 1
- Accept other gases are present in the air (apart from N<sub>2</sub> and O<sub>2</sub>)*
- Accept temperature inside engine may be less than 1500K*
- Accept actual (total) pressure may be less than that assumed*

43.  $[C_6H_5CO_2H] = (1/5 \times 0.010 \Rightarrow) 0.002(0) \text{ mol dm}^{-3}$   
 $[C_6H_5CO_2^-] = (4/5 \times 0.020 \Rightarrow) 0.016 \text{ mol dm}^{-3}$

Accept  $pK_a = 4.20$  (1)

Both correct (1)

Accept  $\frac{0.002}{0.016}$  (1)

$$[H^+] (= K_a \times [C_6H_5CO_2H] / [C_6H_5CO_2^-])$$

$$= 6.3 \times 10^{-5} \times 0.0020 / 0.016$$

$$= 7.875 \times 10^{-6} \text{ (1)}$$

Accept  $pH = (4.20 + 0.90) = 5.1 / 5.10$  (1)

Do not penalise SF for the first two marks

$$pH = -\log[H^+] = 5.1 / 5.10 \text{ (1)}$$

Mark for final answer must be dependant on valid working

e.g. correct [acid]/[base] ratio.

Correct answer with no working (1)

**Allow internal TE**

e.g. an  $\frac{[acid]}{[base]}$  ratio of  $0.010/0.020$  leads to a pH of 4.50 (2)

Reject 5.104 or 5

Reject 1 or >3 sig. fig.

[3]

44. (a)  $K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}}$

IGNORE UNITS HERE

1

Reject [ ]

(b) (i)  $p_{NO_2} = 0.8 \times 1.1$   
 $= 0.88 \text{ (atm)}$

**and**

$$p_{N_2O_2} = 0.2 \times 1.1$$

$$= 0.22 \text{ (atm) (1)}$$

$$K_p = \frac{(0.88)^2}{(0.22)}$$

$$K_p = 3.52 \text{ (1)}$$

$$\text{atm (1)}$$

SECOND MARK IS CQ ON PARTIAL PRESSURES  
AS CALCULATED

3

(ii) **First mark:**  
 $X_{N_2O_4} = 0.10$

$$X_{NO_2} = 0.90 \text{ (1)}$$

*Reject B*

**Second mark:**

$K_p$  constant or

use of  $K_p = 3.52$  or

use of  $K_p$  calculated in (b)(i) (1)

**Third mark:**

Value of  $P_T$  with some working e.g.

$$3.52 = \frac{(X_{NO_2} \times P_T)^2}{X_{N_2O_4} \times P_T}$$

$$3.52 = \frac{0.81}{0.10} \times P_T$$

$$P_T = 0.435 \text{ (atm) (1)}$$

*Mark CQ on first and second answers to (b)(ii)*

*Accept in range 0.43 to 0.44*

**THIRD MARK NOT AVAILABLE IF  $K_p$  EXPRESSION**

**DOES NOT CONTAIN A  $p^2$  TERM**

3

- (c) (i) Increases / gets larger/ gets bigger/ goes up/greater

1

*Reject more*

- (ii) **First mark:**

Fraction/quotient/  $\frac{p_{NO_2}^2}{p_{N_2O_4}}$  /numerator has to increase

(to equal new  $K_p$ ) (1)

**Second mark (can only be awarded for an answer that refers to the fraction/quotient above):**

**EITHER**

so shifts to **RIGHT** hand side (as  $p_{NO_2} \uparrow$  and  $p_{N_2O_4} \downarrow$ ) /

goes in forward direction (as  $p_{NO_2} \uparrow$  and  $p_{N_2O_4} \downarrow$ )

**OR**

so (more)  $N_2O_4$  changes to  $NO_2$

**OR**

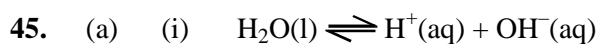
so (equilibrium) yield of  $NO_2$  increases (1)

2

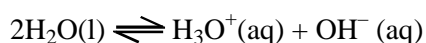
*Mark consequentially on "decreases" in (i)*

*Le Chatelier argument scores (0)*

[10]

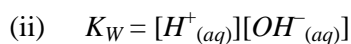


**OR**

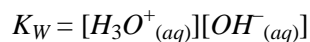


IGNORE STATE SYMBOLS 1

Reject if a **full** arrow is shown in the equation



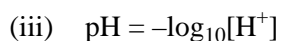
**OR**



IGNORE STATE SYMBOLS 1

If  $[H_2O]$  included (0).

Reject  $K_w = [H^+]^2$



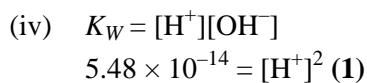
**OR**



**OR**

in words 1

Accept  $pH = \lg 1/[H^+]$



$$[H^+] = \sqrt{5.48 \times 10^{-14}}$$

$$[H^+] = 2.34 \times 10^{-7} \text{ (mol dm}^{-3}\text{)}$$

$$pH = 6.6(3)$$
 (1)

correct answer with no working (2) 2

$pH = 13.3/13.6$  scores (0)

(v) (In pure water)

$$[H^+] = [OH^-]$$

**OR**

equal **concentrations** of  $H^+$  and  $OH^-$  1

(b) (i) 12.5 1

- (ii) 4.8 / 4.9  
[no consequential marking from (i)] 1

*Reject 5 or 5.0*

(iii) 
$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

**OR**

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$
 1

*Reject expressions containing [H<sub>2</sub>O]*

*OR*

*Reject "HA"*

*generic equations*

- (iv) (at half-neutralised point so)

$pK_a = 4.8$

*Mark CQ on (ii)*

*Reject just pH = 4.8 as already credited in (b)(ii)*

**OR**

$pH = pK_a$  (1)

$K_a = \text{antilog}_{10}(-4.8)$

$K_a = 1.6 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$  (1)

*Mark CQ on pKa*

*Accept if pKa = 4.9, Ka = 1.3 × 10<sup>-5</sup>*

*Reject answers to other than 2 s.f.*

**Must be to two sig figs**

**CORRECT ANSWER WITH OR WITHOUT WORKING (2)** 2

*Reject 2.5 × 10<sup>-9</sup> scores (0)*

- (c) **Phenolphthalein:**  
 changes colour (OWTTE) in vertical part of the graph  
**OR**  
 changes colour within a stated range anywhere from 7 to 11 (1)

*Reject if colour change "pink to colourless"*

**Methyl orange**

changes colour at a low(er) pH

**OR**

has already changed colour

**OR**

changes colour before the vertical (section) (1)

*Allow range for methyl orange of 3 to 6 or colour change takes place below pH = 7*

*Reject **just** 'methyl orange changes colour outside the vertical range'*

[NB There must be a statement about methyl orange for second mark] 2

[13]

46. (a) (i) Liquids are more disordered than solids/ solids are more ordered than liquids/ solids are less disordered than liquids / liquids are less ordered than solids 1

*Accept more ways of arranging energy in a liquid because of translation/rotation energy*

*Reject just "more ways of arranging energy"*

- (ii)  $(165 + 217.1 - 166.5) + 215.6$  OR  $+216$  ( $\text{J mol}^{-1} \text{K}^{-1}$ )  
 "+" sign essential 1

*Accept  $+(0).2156 \text{ kJ mol}^{-1} \text{K}^{-1}$*

*OR  $+0.216 \text{ kJ mol}^{-1} \text{K}^{-1}$*

*Reject  $215 \text{ J mol}^{-1} \text{K}^{-1}$*

*Reject  $0.215 \text{ kJ mol}^{-1} \text{K}^{-1}$*

- (iii) Yes because  
 The products include a gas (1)

*Accept solid goes to liquid and gas for first mark*

One mole/molecule goes to two moles/molecules (1) 2

*1 reactant goes to 2 products does not get 2<sup>nd</sup> mark*

(b)  $\Delta S^{\ominus}_{\text{surroundings}} = \frac{-\Delta H}{T}$

OR

$$\frac{-123800}{298} \quad (1)$$

$$= -415 \text{ J mol}^{-1} \text{ K}^{-1} \quad (1)$$

2

*Accept  $-0.415 \text{ kJ mol}^{-1} \text{ K}^{-1}$*

*Accept  $-415.4 \text{ J mol}^{-1} \text{ K}^{-1}$*

*Accept final answer with no working (2)*

*Allow "j" for "J"*

*Reject full calculator display eg  $-415.4362416$*

*Reject more than 2 dp e.g.  $-415.436$*

(c) (i)  $\Delta S_{\text{total}} = -415 + 216 = -199$   
or  $-199.8$  or  $-200$  ( $\text{J mol}^{-1} \text{ K}^{-1}$ )  
IGNORE 4<sup>th</sup> significant figure

1

*Accept  $-0.199 \text{ kJ mol}^{-1} \text{ K}^{-1}$*

*ALLOW TE from (a)(ii) and (b)*

(ii) reactants predominate / equilibrium lies well to the left

OR

Equilibrium completely to the left

1

*ALLOW TE from (c)(i)*

(d) (i)  $K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} \quad (1)$

IGNORE state symbols or lack of them unless (s) or (l)

Units atm (1)

2

*Accept capital "P"*

*Accept use of ( )*

*If expression the wrong way up allow second mark if units given as  $\text{atm}^{-1}$*

*Reject use of [ ]*

(ii)

Substance	Moles at start	Moles at equilibrium	$P_{\text{eq}}/\text{atm}$
$\text{PCl}_5(\text{g})$	<b>0.20</b> <b>(1)</b>		$\frac{0.15}{0.25} \times 4.32$ $= 2.592$
$\text{PCl}_3(\text{g})$		<b>0.05</b>	$\frac{0.05}{0.25} \times 4.32$ $= 0.864$
$\text{Cl}_2(\text{g})$		<b>0.05</b>	<b>0.864</b>
Total number of moles at equilibrium		<b>0.25</b>	

All three(1)    All three(1)

Allow consequential marking across columns

3

*If moles at eqm are given as 0.025 for  $\text{PCl}_3(\text{g})$  and for  $\text{Cl}_2(\text{g})$  then 4<sup>th</sup> column should be 3.24, 0.54 and 0.54 and gets 2 (out of 3)*

(iii)  $(K_p = \frac{0.864 \times 0.864}{(2.592)})$   
 $= 0.288 \text{ (atm)}$

1

*ALLOW TE from di and from dii*

*Common wrong values above gives 0.090*

*ALLOW 0.29*

*Reject 0.3*

*reject 0.28*

(iv) **A** No change because  $K_p$  depends only on temperature / number of moles would change in same proportion **(1)**

**B** Increase because reaction is endothermic **(1)**

OR

entropy arguments

2

*If both changes correct but no explanations then 1 (out of 2)*

[16]



47. (a) (i)  $K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$  (1)  
 mol dm<sup>-3</sup> (1)  
 If H<sub>2</sub>O is included as denominator then allow only the 2<sup>nd</sup> mark if no units suggested 2
- (ii)  $\text{p}K_a = -\log K_a / -\lg K_a / -\log_{10} K_a$  1  
 Accept  $K_a = 10^{-\text{p}K_a}$
- (b) A solution which does not change its pH value (significantly) (1)  
*May be shown using an equation*  
 When some/small amount of acid or alkali is added (1) 2
- (c) Acting as a base because it is accepting a proton (to form H<sub>2</sub>CO<sub>3</sub>/CO<sub>2</sub> + H<sub>2</sub>O) 1
- (d) (i) Before race  $7.4 = 6.5 - \log \frac{[\text{acid}]}{[\text{base}]}$   
 $\text{Log} \frac{[\text{acid}]}{[\text{base}]} = -0.9$  (1)  
 $\frac{[\text{acid}]}{[\text{base}]} = 0.126$  (1) 2  
 Accept 0.13  
 Reject 0.12
- (ii) Before race  
 $[\text{CO}_2] = 0.126 \times 0.0224 = 2.82 \times 10^{-3}$   
 OR  
 $2.52 \times 10^{-2} - 2.24 \times 10^{-2} = 2.8 \times 10^{-3}$  1

(iii) Hypothesis I would result in an increase in  
 $[\text{CO}_2] / [\text{HCO}_3^-] / [\text{CO}_2 + \text{HCO}_3^-]$   
 OR  
 Hypothesis II would produce greater acidity without  
 additional  $[\text{CO}_2] / [\text{HCO}_3^-] / [\text{CO}_2 + \text{HCO}_3^-]$  (1)  
 The table shows a fall in  $[\text{CO}_2] / [\text{HCO}_3^-] / [\text{CO}_2 + \text{HCO}_3^-]$   
 and therefore Hypothesis II must be favoured. (1)

2

[11]

48. C

[1]

49. C

[1]

50. A

[1]

51. C

[1]

52. (a) C

1

(b) D

1

(c) B

1

[3]

53. (a) A

1

(b) D

1

- (c) C 1
54. (a) methyl butanoate  
Accept Methyl butanoate 1  
*Reject 'an' missing*
- (b) the other three substances can form  
**intermolecular** hydrogen bonds with themselves but the ester cannot. 1  
*Reject Discussion of London Forces*
- (c) Hydrolysis 1
- (d) QWC  
Must cover advantages and disadvantages. Must **not** be contradictory  
**Advantages to manufacturers: (any two)**
- not dependent on weather, seasons etc
  - consistent taste /concentration/more consistent
  - quality
  - or alternative ideas
- Disadvantages to consumers : (any two)**
- some people put off by 'non-natural' food
  - may not taste the same as natural product which may contain other impurities
  - unable to describe the product as organic
- or alternative ideas 4  
*Reject cost with no justification*

(e) 
$$K_c = \frac{[C_3H_7COOH(l)][CH_3OH(l)]}{[C_3H_7COOCH_3(l)][H_2O(l)]} \quad (1)$$

Accept eq subscripts

	Moles at equilibrium	Concentration / mol dm <sup>-3</sup>
<b>butanoic acid</b> = 4.4/88 =	0.05	1.67
<b>methanol</b>	0.05	1.67
<b>ester (methyl butanoate)</b>	0.05	1.67
<b>water</b>	0.95	31.7

all four equilibrium moles = (1)

Conc at equilibrium = equilibrium moles ÷ 0.030 (1)

$$K_c = \frac{1.67 \times 1.67}{1.67 \times 31.7} \quad (1) = 0.053 \quad (1)$$

ignore significant figures unless value given to 1 s.f.

The units cancel because both the top and bottom of the fraction have units of concentration squared.

Or same number of moles on both sides of the equation (1)

5

*Reject absence of square brackets*

[12]

55. (a) Value of equilibrium constant increases (1) 1

(b) QWC

If the equilibrium constant increases then more products will be formed (1)

And the position of equilibrium will move to the right (1)

2

[3]

56. (a)  $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$   
Accept state symbols omitted 1

(b) (i) Positive because a gas is given off (1)  
which is more disordered and so has more entropy (1) 2

(ii) Positive because the reaction is exothermic (1)  
and =  $-\Delta H/T$  (1) 2

(iii) Positive because the reaction occurs / total entropy change  
is the sum of the two positive values above. 1

(c) (i) Surface coated with magnesium oxide (which would react to  
form water rather than hydrogen). 1

(ii) QWC

Initial number of moles of HCl =  $20 \times 1 / 1000 = 0.02$

Number of moles of Mg =  $0.1 / 24 = 0.00417$  (1)

number of moles of HCl which reacts is 0.00834 (1)

Therefore number of moles of HCl left = 0.01166 (1)

Ignore sig figs

so the concentration nearly halves which would significantly reduce the rate and so make the assumption that the initial rate is proportional to 1/time invalid / inaccurate. (1)

Increase the volume of acid to (at least)  $50 \text{ cm}^3$  (1)

Or measure the time to produce less than the full amount of gas

Or use a smaller piece of magnesium. (1)

5

(iii) Energy given out =  $467\,000 \times 0.1 / 24 \text{ J} = 1\,946 \text{ J}$

$20 \times 4.18 \times \Delta T = 1\,946$  (1)

$\Delta T = 23.3^{(0)}$  (1)

Accept units of degrees celsius or Kelvin

This temperature change would significantly increase the rate of the reaction (1)

Carry out the reaction in a water bath of constant

temperature/use a larger volume of more dilute acid (1)

4

(iv) At 329 time 4s  $1/\text{time} = 0.25 \text{ s}^{-1}$   $\ln(\text{rate}) = -1.39$  (1)

At 283 time 124s  $1/\text{time} = 0.00806 \text{ s}^{-1}$   $\ln(\text{rate}) = -4.82$  (1)

[graph to be drawn]

Plot line with new gradient =  $-3.43 / 0.00049$

=  $-7\,000$  (1)

Accept  $-6800$  to  $-7200$

Activation energy =  $+7\,000 \times 8.31$

=  $+58.2 \text{ kJ mol}^{-1}$  (1)

4

(v) QWC

Rate of reaction reduced because less surface area in contact with the acid. (1)

1

- (vi) Any two
- Repeat the experiment at each of the temperatures
  - obtain an initial rate eg by measuring the volume of gas given off before the reaction is complete.
  - Other sensible suggestions.
- 2
- (vii) The rate should be lower, since ethanoic acid is a weaker acid (compared to hydrochloric acid) and so there will be a lower concentration of hydrogen ions present.
- 1

[24]

### 57. QWC

Answer must be given in a logical order, addressing all the points using precise terminology

- Collision **frequency** increases as particles moving more quickly (1)
  - More collisions have sufficient energy to overcome activation energy / more molecules on collision have energy  $\geq$  activation energy (1)
  - A greater **proportion** of collisions result in reaction (1)
  - Collision energy has greater effect (1)
  - Homogeneous all in same phase and heterogeneous in different phases / gas and solid (1)
  - No need to separate products from catalyst (1)
- 6

*Reject more collisions*

*Reject more successful collisions*

[6]