1. (a) (i) $2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$
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)**

$CaO + H_2O \rightarrow Ca(OH)_2$ **(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 N_2O_4 **(1)** 2

(iii) $$K_p = \frac{p(NO_2)^2}{p(N_2O_4)}$$

There must be some symbolism for pressure, and no [ ] 1

(iv) $$\left(K_p = \frac{p(NO_2)^2}{p(N_2O_4)} = 48\right)$$

$p(NO_2)^2 = 48 \times 0.15 = 7.2$ **(1)**
$p(NO_2) = 2.7$ **(1)** atm **(1)** accept 2.683 / 2.68 / 2.7

Answer and units conditional on (iii). 3

[16]

2. (a) (i) HCl: pH = 1.13

$\therefore [H^+] = 0.074\ \text{mol dm}^{-3}$

$\therefore [HCl] = 0.074\ \text{mol dm}^{-3}$ [0.074 to 0.07413] 1

(ii) HOCl: pH = 4.23

$\therefore [H^+] = 5.89 \times 10^{-5}\ \text{mol dm}^{-3}$ **(1)**

$K_a = \dfrac{[H^+]\,[OCl^-]}{[HOCl]}$ **(1)**

$[H^+] = [OCl^-]$ **(1)** or implied later in calculation

$[HOCl] = [H^+]^2 / K_a = 0.0932\ \text{mol dm}^{-3}$ **(1)** 4

(b) (i) $[H^+] = 0.10 / 0.1047 / 0.105$ **(1)**

(ii) $H_2SO_4 \rightarrow H^+ + HSO_4^-$ **(1)** $\rightarrow$ or $\rightleftharpoons$

$H_2SO_4 + H_2O \rightarrow H_3{}^+O + HSO_4^-$ ignore state symbols

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ **(1)** Must be $\rightleftharpoons$

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ ignore state symbols

(iii) second ionisation suppressed by the first ionisation **(1)** 4

(c) (i) $K_c = \dfrac{[Cl_2]^2 \times [H_2O]^2}{[HCl]^4 \times [O_2]}$ 1

(ii) $4HCl \quad + \quad O_2 \quad\quad 2Cl_2 \quad + \quad 2H_2O$

equilibrium mols 0.20 0.050 **(1)** 0.30 and 0.30 **(1)**

[ ] eq ÷ 10 **(1)** 0.020 0.0050 0.030 0.030

$K_c = \dfrac{[0.030]^2 \text{ x } [0.030]^2}{[0.020]^4 \text{ x } [0.005]} = 1010$ or 1012 or 1013 or 1012.5 $(\text{mol}^{-1}\ \text{dm}^3)$ **(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_2 / to endothermic / lower yield **(1)**
Press	Increases/faster **(1)**	Right to SO_3 / 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_3 **(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_3 / 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_2O_5 **(1)** 1

(e) Any one use
production of fertilizers, detergents, dyes, paints, pharmaceuticals (in) car batteries, pickling metal 1

[13]

4. (a) only partially dissociated / ionised / not fully dissociated **(1)**
into H^+ ions / $H_3{}^+O$ / proton donor **(1)** 2

(b) $K\text{a} = \frac{[H_3O^+][A^-]}{[HA]}$ **(1)** 1

(c) (i) 9.0 to 9.4 **(1)** 1

(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)**
indictor 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) $Kp = \frac{P_{SO2}{}^2 \times P_{O2}}{P_{SO3}{}^2}$ **(1)**

[ ] no mark
( ) OK 1

(ii)	$2SO_3$	$\rightarrow$	$2SO_2$	$+$	O_2	
Mols at start	2		0		0	
mols at equ	0.5		1.5		0.75	**(1)**

Mark by process
1 mark for working out mole fraction
1 mark for × 10
1 mark for correct substitution in K_p and answer
1 mark for unit

i.e. $P_{SO2} = \frac{1.5}{2.75} \times 10 = 5.46$

$P_{O2} = \frac{0.7}{2.75} \times 10 = 2.73$

$P_{SO3} = \frac{0.5}{2.75} \times 10 = 1.83$

n.b. could show mole fraction for all 3 and <u>*then*</u> *× 10 later to give partial pressure.*

Kp = $(5.46)^2 \times (2.73) / (1.83)^2 = 24.5$ **(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_{total} × mol fraction **(1)** 1

(ii) $K_p = \frac{p(CO) \times p(H_2)^3}{p(CH_4) \times p(H_2O)}$ **(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) $K_p = \frac{1}{p(CH_4)}$ **(1)** 1

(ii) 9.87×10^{-3} kPa^{-1}/ 9.87×10^{-6} 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

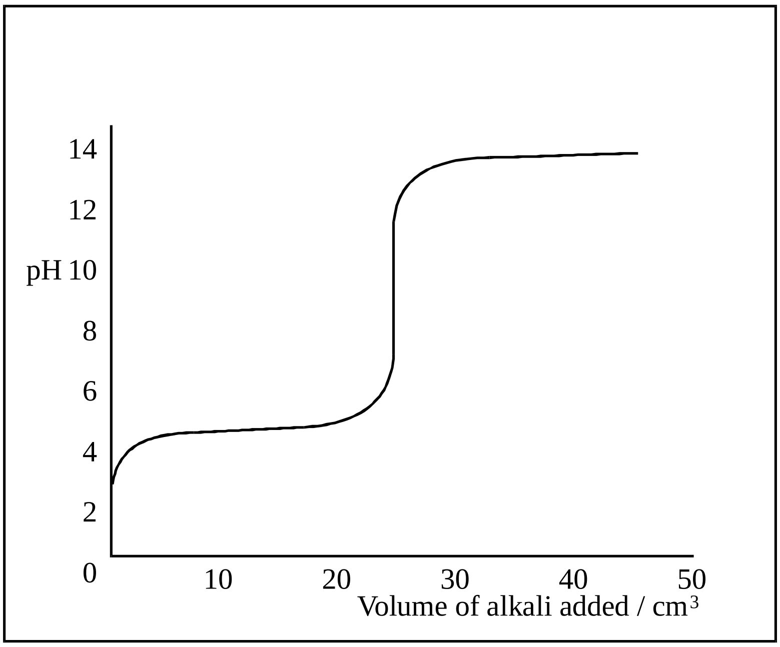
(iv) Answer yes or no with some sensible justification **(1)**
e.g. No the costs would not justify the amount produced 1

[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^3
general shape **(1)** finish above 12 4

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

(e) (i) $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ **(1)**

or

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

(ii) pH = pK_a at half way to neutralisation point = 12.5 cm^3 **(1)**
This could be shown on the graph
because pH = pK_a when $[CH_3COO^-] = [CH_3COOH]$ **(1)** 2

[11]

8. (a) The marks are for:

- writing the expression for K
- substituting correctly
- calculating p(SO_3)
- correct generation of the ratio
- calculation of the ratio to give answer which rounds to 95 t

Kp = $pSO_3^2 / pSO_2^2 \times pO_2$ (= 3.00×10^4) **(1)**
$3.00 \times 10^4 = pSO_3^2 / 0.1 \times 0.1 \times 0.5$ **(1)** *if no expression for Kp is given this correct substitution can score 2 marks*

$pSO_3^2 = 150$
$pSO_3 = 12.25$ **(1)**
Ratio of $SO_3 = \frac{12.25 \times 100\%}{(12.25 + 0.1 + 0.5)}$ **(1)** = 95% **(1)** 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) pH = $-\log_{10}(0.200) = 0.70$ **(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 H^+ from the first **(1)**

little contribution from 2nd ionisation so reduces the pH very little / increases the $[H^+]$ very little **(1)** 3

(d) (i) Lead equations 1 mark
$Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e^-$ **(1)**
or
$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Lead(IV) oxide equations 2 marks
$PbO_2 + H_2SO_4 + {}_2H^+ + 2e^- \rightarrow PbSO_4 + {}_2H_2O$
or
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O+$
Species **(1)** balancing **(1)** 3

(ii) $PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$ (1) 1

[18]

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

(ii) $K_W = [H^+] [OH^-]$ or $K_W = [H_3{}^+O] [OH^-]$ **(1)** 1

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

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

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

(d) (i) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ **(1)** 1
allow $[H_3{}^+O]$

(ii) $[H^+] = \sqrt{} (K_a \times [HA])$ **(1)** = 0.00474 **(1)**
pH = 2.32 / 2.33 **(1)** 3

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

$\text{pH} = \text{p}K_a + \log\dfrac{[A^-]}{[HA]}$

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

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) $\dfrac{0.2}{30}$ $\dfrac{0.1}{60}$ $\dfrac{1.8}{60}$

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

$K_c = \dfrac{(0.03)^2}{(3.33 \times 10^{-3})^2 \times 1.67 \times 10^{-3}}$ = 4860or 4.86×10^{-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; 1
SO_3 = 1.71(4) atm **(1)** i.e. multiply answer in (ii) by 2

(iv) $1.714^2 / 0.1905^2 \times 0.09524 = 850$ **(1)**

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)**

$ZnCO_3$ has more atoms/is more complex than ZnO **(1)** 2

(ii) $\Delta S^{\ominus}_{system} = (+43.6) + (+213.6) - (+82.4)$

$= +174.8/175\ \text{J mol}^{-1}\ \text{K}^{-1}$

method **(1)**
answer, sign and units **(1)**
Correct answer, sign and units with no working **(2)** 2

(b)

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

ONLY accept 3 or 4 SF 2

IF correct answer, sign and units with no working ***(1)***

(c) (i)

$\Delta S^{\ominus}_{total} = +174.8 - 1558.7$	
$= -1384 / -1380\ \text{J mol}^{-1}\ \text{K}^{-1}$	$= -63.5 / 64 / 63 / 63.2 / 63.4\ \text{J mol}^{-1}\ \text{K}^{-1}$
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 $\Delta S^{\ominus}_{total}$ /**total entropy change**

is negative / less than zero. 1

MUST be consistent with (i)

(d) (i) $K_p = p\ co_2$ ((g) eqm) 1

(ii) Increase temperature / reduce pressure **(1)**
Decreases $\Delta S^{\ominus}_{surroundings}$ (negative) and hence increases $\Delta S^{\ominus}_{total}$ / Le Chatelier's principle applied (i.e increasing temperature, reducing pressure) **(1)** 2

[11]

12. (a) (i) Pairs up CH_3CH_2COOH and $CH_3CH_2COO^-$
and H_2O/H_3O^+**(1)**; correct identification of which is acid and which base **(1)** 2

(ii) $K_a = [CH_3CH_2COO^-][H_3O^+] / [CH_3CH_2COOH]$ **(1)** 1

$[H^+]$ is acceptable.

(iii) $[H^+] = (Ka[HA])^{½}$ or $\sqrt{Ka[HA]}$ **(1)** = $(1.\ 3 \times 10^{-5} \times 0.10)^{½}$
$= 1.14 \times 10^{-3}$ 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 [H+] provided the pH resulting is between 0 and 7.

(iv) $[H^+][OH^-] = 10^{-14}$ **(1) =** $1.14 \times 10^{-3}\ [OH^-]$
Thus $[OH^-] = 10^{-14} \times 10^{-3}$ **(1)**
= $8.77\ (8.8) \times 10^{-12}$ mol dm^{-3} **(1)** units needed (2 or 3 sf)
Consequential on the answer to (iii) for $[H^+]$
Allow 8.71×10^{-12} if solved using pH + pOH and pH = 2.94;
7.9×10^{-12} if solved using pH + pOH and pH = 2.9. 3

(b) $CH_3CH_2COO^- + H_2O \rightleftharpoons CH_3CH_2COOH + OH$ **(1)**
Hydroxide ions make the solution alkaline **(1)** or propanoate ion deprotonates the water

or $CH_3CH_2COONa + H_2O \rightarrow CH_3CH_2COOH + NaOH$ **(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) pH = p*K*a + lg [salt]/[acid] **(1)**
= 4.9 + Ig (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

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

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

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) pH = **–**Ig [H^+(aq)]
OR [H^+(aq)] = $10^{-\mathrm{pH}}$ / $10^{-9.6}$ = $10^{-9.6}$ (method) **(1)**
= 2.5(1) × 10^{-10} **mol dm** $^{-3}$ **(2)** 3

(b) (i) $K_w = [H^+(aq)][OH^-(aq)]$ 1

(ii) $[\mathrm{OH}^-\ (\mathrm{aq})] = \dfrac{K_w}{\left[\mathrm{H}^+(\mathrm{aq})\right]}$

$$= \frac{1.0 \times 10^{-14}}{2.51 \times 10^{-10}}$$

= 3.98 / 4(.0) × 10^{-5} mol dm^{-3} 1

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

(iv) =1.99 / 2(.03) ×10^{-5} × 74
=0.00147 (g dm^{-3}) 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 $Ca(OH)_2 = \frac{100 \times 1.99 \times 10^{-5}}{1000}$

$= 1.99 \times 10^{-6}$ mol **(1)**

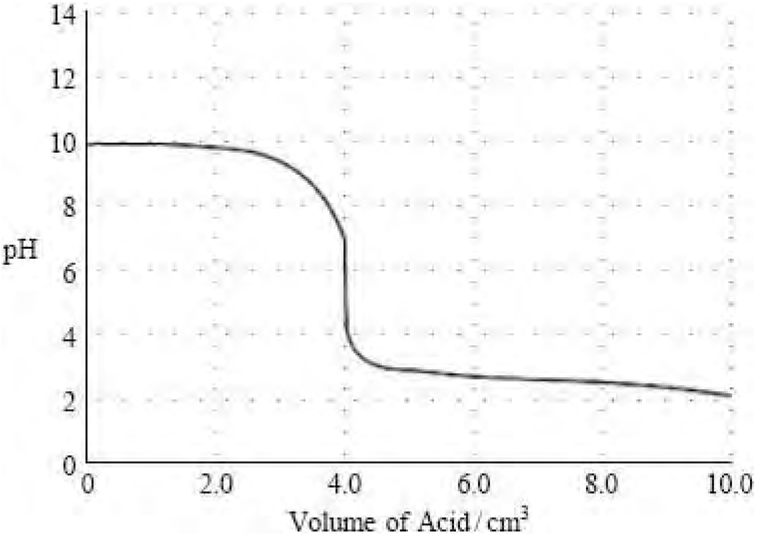
$\therefore$ Amount of HCl = $\frac{2 \times 100 \times 1.99 \times 10^{-5}}{1000}$

$= 3.98 \times 10^{-6}$ mol **(1)**

$\therefore$ Volume of HCl = $\frac{1000 \times 2 \times 100 \times 1.99 \times 10^{-5}}{1000}$

= 4(.0) / 3.98 cm^3 *OR* 4(.0) / 3.98 × 10^{-3} dm^3 **(1)** 3

(iii)



Vertical portion of the graph (between pH 7 and 4) at about 4 cm^3 **(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) NH_3 base and NH_4^+ acid **(1)**

H_2O acid and 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^3 **(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 / $pK_{ind} \pm 1$ 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) $$K_a = \frac{[H_3O^+]\times[NO_2]}{[HNO_2]}$$
square brackets essential 1

(ii) $[H^+] = [NO_2^-]$ or $[H^+]^2 = K_a \times [HNO_2]$ **(1)**
$[H^+] = \sqrt{(K_a \times 0.12)} = 0.00751$ mol dm^{-3} **(1)**
pH = $-\log[H^+] = 2.12/2.1$ **(1)**
ALLOW any correct conversion of $[H^+$*l into pH provided the answer is less than 7* 3

(iii) Moles $NaNO_2 = 1.38/69 = 0.020$ **(1)**
$[NO_2^-] = 0.020 / 0.10 = 0.20$ (mol dm^{-3})
$[H^+] = \frac{K_a[\text{acid}]}{[\text{salt}]} = \frac{4.70\times10^{-4}\times0.120}{0.20} = 2.82\times10^{-4}$ **(1)**
pH = $-\log 2.82\times10^{-4} = 3.55/3.6/3.5$ **(1)** 4

(iv) In a buffer both [acid] and [salt] must be large compared to the added H^+ or OH^- ions **(1)**
but in $NaNO_2$ alone $[HNO_2]$ is very small **(1)**
OR
to remove both H^+ and OH^- there must be a large reservoir of both NO_2^- ions and HNO_2 molecules **(1)**
which there are a solution of $NaNO_2$ and HNO_2 but not in NaNO alone **(1)** 2

[18]

15. (a) Pressure *NOT* partial pressure)
intensity or change of colour) *Any one*
volume) 1

(b) $K_c = [NO_2(g)]^2 / [N_2O_4(g)]$
State symbols required 1

(c) Mol NO_2 at equilibrium = 0.0120 / 1.20×10^{-2} **(1)**
$K_c = (0.0120)^2 \div (0.0310)$
= 4.6 / 4.65×10^{-3} **(1)** mol dm^{-3} **(1)** 3

(d) (i) Amount of NO_2 reduced 1

(ii) No effect 1

(e) As K_c is bigger, more NO_2 is produced so heat helps forward reaction /
by Le Chatelier's principle reaction goes forward to use up heat /
as temperature increases ΔS_{total} must be more positive so $\Delta S_{surroundings}$
(= $-\Delta H/T$ must be less negative 1

(f) Positive / + *with some attempt at explanation* **(1)**
1 mol / molecule gas → 2 mol / molecule gas / products more disordered than reactants **(1)** 2

(g) $\Delta S_{surroundings} = -\frac{\Delta H}{T}$ OR $\frac{-\Delta H \times 1000}{T}$ 1

(h) ΔS_{total} is positive as reaction occurs **(1)**
So ΔS_{system} must be more positive than $\Delta S_{surroundings}$ is negative **(1)** 2

[13]

16. (a) (i) pH = $-\log_{(10)} [H_3O^+]$ **(1)**
OR $[H^+]$ *instead of* $[H_3O^+]$ *applied throughout* 1

(ii) $[H_3O^+]$ greater than 1 (mol dm^{-3}) 1

(b) (i) $K_a. = \dfrac{[H_3O^+][A^-]}{[HA]}$ **(1)**

$[H_3O^+] = 1.14 \times 10^{-3}$ mol dm $^{-3}$ **(1)**

pH = 2.9(4) **(1)** 3

(ii) Start at the same pH as in (i) **(1)**

Graph showing vertical at 25 cm^3 **(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_a 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) $K_p = \dfrac{p(N_2)p(O_2)}{p(NO)^2}$ 1

(ii) Correct number of moles **(1)**

Correct mole fractions **(1)**

Correct partial pressures **(1)**

2.45×10^3 **(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) $K_p = p\,(Ni(CO)_4) / p(CO)^4$ 1

(ii) High partial pressure *with some reason* **(1)**

so the pressure $Ni(CO)_4$ increases to keep Kp constant. **(1)** 2

[12]

18. (a) (i) Methanol is the biggest/ most complex molecule / greatest M_R /most atoms/most electrons 1

(ii) $\Delta S_{system} = 239.7 - 197.6 - 2(130.6)$

$= -219.1 / -219 \text{ J mol}^{-1}\text{K}^{-1}$

Method **(1)**

answer + units **(1)** 2

(iii) yes as 3 molecules → 1 *OR* yes as (2) gases → a liquid 1

(iv) $\Delta S_{surr} = -\Delta H/T$ (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) $\Delta S_{total} = -219.1 + 433 = +213.9 / +213.8 \text{ J mol}^{-1} \text{K}^{-1}/ +214 \text{ J mol}^{-1} \text{K}^{-1}/ +0.214 \text{ kJ mol}^{-1}\text{K}^{-1}$ **(1)**

Positive so **possible (1)** 2

(b) (i) <u>Temperature</u>

Faster at 400°C **(1)**

even though yield is lower **(1)**

<u>Pressure</u>

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) $K_p = p(CH_3OH)/p(CO)\times p(H_2)^2$ 1

(iv) Partial pressure of methanol = 200 – 55 – 20 = 125 atm **(1)**

$K_p = (125)/55\times20^2$

$= 5.68 \times 10^{-3} / 5.7 \times 10^{-3} \text{ atm}^{-2}$ **(1)** 2

(c) (i) Number of molecules / fraction of molecules with energy ≥ 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

[17]

19. (i) Weak acid is dissociated to a small extent/slightly dissociated/ ionised/few molecules dissociate

ALLOW partial dissociation

NOT ‘not fully dissociated’. 1

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

(iii) Ka = $[H_3O^+]^2$ / [acid] *OR* $[H_3O^+] = \sqrt{}$ Ka [acid] **(1)**
$[H_3O^+] = 1.23 \times 10^{-3}$ **(1)** – *dependent on 1st 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 2nd or 3rd boxes above pH 2* **(1)**
consequential on (iii)
pH range vertical max 6 to 12 min 7–10 **(1)**
Equivalence point at $25cm^3$ **(1)**
General shape of curve **and** finish at pH between 12–13 **(1)** –
and end in 1st three boxes above 12, extending to 40–50 cm^3

*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) (2×192.3)–[191.6 + (130.6 × 3)] **(1)**
= –198.8/199 J mol^{-1} K^{-1} **(1)** 2

(b) $\frac{--92.2\times1000/}{298}$ $\frac{--92.2/}{298}$ $-\Delta H /_{T}$ **(1)**
= + 309(.4) J mol^{-1} K^{-1} / + 0.309(4) kJ $mol^{-1}K^{-1}$ **(1)** 2

(c) (i) –198.8 + 309 = + 110 J mol^{-1} K^{-1} (3 SF)
OR
– 198.8 + 309.4 = + 111 J mol^{-1} 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 ΔS_{total} is positive / total **entropy change** 1

(d) (i) Higher T makes $\Delta S_{surroundings}$ decrease (so ΔS_{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) $K_P = p(CO_2)$ *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* atm^{-1} 1

(b) (i) $K_p = \frac{p(Cl_2) \times p(NO)^2}{(p(NOCl))^2}$ *allow without brackets, penalise* [ ] 1

(ii) $2NOCl \rightleftharpoons 2NO + Cl_2$

	2NOCl	2NO	Cl_2	
Start	1	0	0	
Δ	–0.22	+0.22	+0.11	
eq moles	0.78	0.22	0.11	**(1)**

total moles of gas 1.11

mole fractions above values ÷1.11 **(1)**

0.7027	0.1982	0.09910

partial pressure / atm above values × 5.00 **(1)**

3.51	0.991	0.495

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

= 0.0395/ 0.0394 atm **(1)**

range of answers 0.0408 / 0.041 → 0.039 / 0.0392 NOT 0.04
ACCEPT ≥ 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 1st 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 / ΔH_{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
ΔH for $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+ = +2 kJ\ mol^{-1}$ / almost zero / very small **(1)**
$\therefore \Delta H_{neut} [CH_3COOH] = +2 + \Delta H_{neut} [HCl]$ **(1)**
≈ the same (for both acids) **(1)**
OR
ΔH_{neut} is per mole of H_2O produced **(1)**
(heat) energy required for full dissociation (of weak acid) **(1)**
so ΔH_{neut} slightly less exothermic (for weak acid) **(1)** 3

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

$[H^+] = 0.00156$ (mol dm^{-3}) **(1)**
pH = 2.81 *consequential on $[H^+]$ but not pH>7* **(1)**
ACCEPT 2.80/2.8 (answers to 1 or 2 dp)

The assumptions are **two** from:
$[H^+] = [CH_3COO^-]$ – *this mark can be earned from working /*
negligible $[H^+]$ from ionisation of water **(1)**

$[CH_3COOH] = 0.140 - [H^+] \approx 0.140$ (mol dm^{-3}) / ionisation of acid negligible **(1)**
solution at 25°C **(1) max 2** 4

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

$[H^+] = 1.74 \times 10^{-5} \times \dfrac{0.070}{0.100} = 1.22 \times 10^{-5}$ **(1)**
pH = 4.91 / 4.9 / 4.92 *NOT 5*
Max 2 *if 0.140 / 0.200 is used* **(1)** 3

[14]

23. (a) (i) +313.4 − 4 × 197.6 − 29.9 **(1)** Absence of 4 × **(0)**

= –506.9 J mol^{-1}K^{-1} *OR* –507 J mol^{-1}K^{-1} *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 → 1 mole] 1

(iii) $\Delta S^\ominus_{surroundings}$ = –ΔH/T **(1)** For equation or use of equation
= 191 000 / 323
= (+) 591 J mol^{-1}K^{-1} **(1)** *OR* answer in kJ 2

ALLOW (+) 591.3 J mol^{-1} K^{-1} / (+) 590 J mol^{-1} 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) $\Delta S^\ominus_{total}$ is positive/(+84 J mol^{-1}K^{-1}) so reaction should go forwards
ALLOW TE from (a)(i) 1

(b) (i) $K_p = \dfrac{pNi(CO)_4}{pco^4}$ if square brackets [ ] are used **(0)** 1

(ii) $Ni(CO)_4$ moles at eq 0.25 **(1)**
total number of moles = 99.25

$$P_{Ni(CO)4} = \frac{0.25}{99.25} \times 1 = (0.00252)\ P_{CO} = \frac{99}{99.25} = (0.9975)\ \textbf{(1)}$$

2nd 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
= 2.54×10^{-3} **(1)** atm^{-3} **(1)**

Units marked independently
ALLOW 2.5 × 10^{-3}
Many have total number of moles as 100 even when it is not – ALLOW TE for 2nd and 3rd mark if it should be 100 or just TE for third mark if it shouldn't be 100 from their working
[Kp = 2.6 or 2.60 × 10^{-3}] 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 $\Delta S^{\ominus}_{surroundings}$ will become less positive/more negative as the temperature is increased (and ΔS_{system} will remain almost unchanged) so ΔS_{total} becomes negative for the forward reaction **(1)** 2

[16]

24. (a) starts at 2.2 **(1)**
vertical section at 40cm^3 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 2nd and 3rd 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) $[\mathrm{H}^+] = \dfrac{Ka[acid]}{[salt]}$ *OR* $\mathrm{pH} = \mathrm{p}K_a - \lg\dfrac{[\text{acid}]}{[\text{salt}]}$ **(1)**

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

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

pH = 3.4(5) **(1)**
IGNORE no. of decimal places but penalise pH = 3

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

$\mathrm{HA} + \mathrm{OH}^- \rightarrow \mathrm{A}^- + \mathrm{H_2O}$ **(1)**
ALLOW $\mathrm{H}^+ + \mathrm{OH}^- \rightarrow \mathrm{H_2O}$ followed by more dissociation of HA

$\mathrm{A}^- + \mathrm{H}^+ \rightarrow \mathrm{HA}$ **(1)**

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

NOTE: If no equations given for effect of adding OH$^-$ and H$^+$, 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)**

$\Delta S_{\text{surroundings}} = -\dfrac{\Delta H}{\mathrm{T}}$ [*OR given in words*]

OR

$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ [*OR given in words*]
as reaction goes, ΔS_{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) $$(\text{Kp}) = \frac{P_{NO_2}{}^{2}}{P_{NO}{}^{2} \times P_{O_2}}$$ **(1)**

Check that it is ***not*** *a "+" on denominator.*
ALLOW ( ) but NOT [ ] eg *ALLOW* $((P_{NO_2})^2)^2$ etc
ALLOW $(pNO_2)^2$

Atm^{-1} / Pa^{-1} / kPa^{-1} / $m^2\ N^{-1}$ **(1) –** *2nd mark dependent on 1st*
ALLOW $atms^{-1}$ / $atmospheres^{-1}$
NOT atm^{-}*etc*
NOT 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 NO_2 acidic **and** others not **(1 max)**

NOT dilatometry
NOT temperature 2

(ii) [NO] second order **(1)**

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

$[O_2]$ first order **(1)** 3

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

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

rate = k$[NO]^2[O_2]$ rate = k$[NO][O_2]$ 1

(iv) third / 3 second / 2 1

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

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

[20]

26. (a) (i) - lg (0.05) = 1.3(0) 1

IGNORE sig figs from this point on in this question

(ii) $[OH^-] = 1 \times 10^{-14} / 0.05 = 2 \times 10^{-13}$ (mol dm^{-3}) 1

OR via pOH

*Correct answer with no working **(1)***

(b) (i) $K_a = [H_2PO_4^-][H_3O^+]/[H_3PO_4]$
NOT using H^+ instead of H_3O^+ 1

(ii) $[H_3O^+] = 10^{-1.20}$
= 0.063 (mol dm^{-3}) **(1)**

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

$= 9.08 \times 10^{-3}$ **(1)** mol dm^{-3} **(1)**
$= 9.11 \times 10^{-3}$ if $[H_3O^+]$ not rounded

ALLOW

$$K_a = \frac{0.063^2}{0.500}$$ **(1)**

$= 7.94 \times 10^{-3}$ **(1)** mol dm^{-3} **(1)**
$= 7.96 \times 10^{-3}$ if $[H_3O^+]$ 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 cm^3) **(1)**

remove some solution – either with a pipette
OR a known volume / 20 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 ÷ 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

N≡N (+)945 6N–H (–)2346 **(1)**

and

3H–H $\frac{(+)1308}{(+)2253}$ **(1)**

ΔH = 945 +1308 – 2346

= –93 sign and value **(1)**

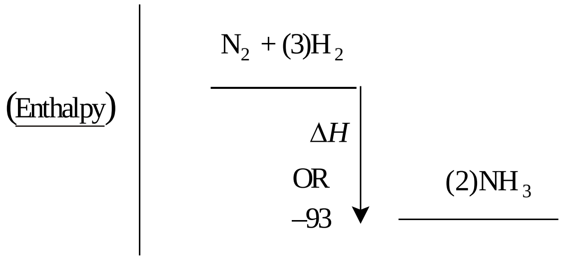
$\Delta H^{\ominus} = -\frac{93}{2} = -46.5$ (kJ mol^{-1})

sign and value q on 3rd mark **(1)** 4

Accept –46.5 (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

ΔH labelled **(1)**
direction of arrow must agree with thermicity

Accept double headed arrow

Diagram marks cq on sign and value of ΔH 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 ΔH_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) <u>advantage</u>
higher (equilibrium) yield/more NH3 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) <u>disadvantage</u>
(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

[18]

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

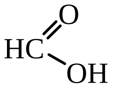
Accept **…** $\rightarrow 2HCOONa(aq) + H_2CO_3(aq)$

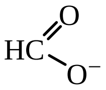
Accept HCO_2H *for the acid*

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

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

Must use square brackets 1

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

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

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

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

$[H^+] = \sqrt{1.60 \times 10^{-4} \times 0.100}$
$= 4.0 \times 10^{-3}$ (mol dm^{-3}) **(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 **(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

$pK_a = 3.80$ **(1)**

$pH = \frac{1}{2}pK_a - \frac{1}{2}\log[\text{acid}]$ **(1)**
pH = 1.90 – (–0.50)

pH = 2.40 **(1)** 3

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

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

OR

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

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

Reject $\dfrac{0.100}{0.400}$

pH = 4.40 **(1)** IGNORE sig figs

Reject 4.39 (rounding error) so no third mark

OR

$pH = pK_a - \log_{10}\left\{\dfrac{[HCOOH]}{[HCOO^-]}\right\}$ **(1)**

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

Reject $\dfrac{0.100}{0.400}$

pH = 3.80 – (–0.60)
pH = 4.40 **(1)** IGNORE sig figs 3

Reject 4.39 (rounding error) so no third mark

(ii) Addition of H^+ ions:
$HCOO^- + H^+ \rightarrow HCOOH$ **(1)**

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

Addition of OH^- ions:
$HCOOH + OH^- \rightarrow HCOO^- + H_2O$ **(1)**

If the ionisation of sodium methanoate shown with $\rightleftharpoons$ then **max (1)** out of 2 for above equations

Addition of OH^- *ions:*
$H^+ + OH^- \rightarrow H_2O$ ***must be*** *followed by more dissociation of HCOOH (to restore* $[H^+]$*)*

Accept "molecular" equations or equations described in words or notation involving HA, H^+ *and* A^-.

(buffer solution has) high concentrations
Or a large reservoir of **both** *HCOOH* **and** $HCOO^-$
relative to added H^+ / OH^- **(1)**
(hence virtually no change in $[H^+]$) 3

Accept just "large reservoir of both HCOOH and $HCOO^-$*"*

[16]

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

(i) **moles SO_2** (10.0 – 9.00) = 1.00 (mol)
moles O_2 (5.00 – 4.50) = 0.500 (mol)
moles SO_3 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.

$$X_{SO_2} = \frac{1.00}{10.5} (= 0.0952) \text{ or } {}^{2}\!/_{21}$$

$$X_{O_2} = \frac{0.500}{10.5} (= 0.0476) \text{ or } {}^{1}\!/_{21}$$

$$X_{SO_3} = \frac{9.00}{10.5} (-0.857) \text{ or } {}^{18}\!/_{21} \text{ or } {}^{6}\!/_{7}$$

Reject rounding to 1 sig fig

Mark consequential on (a)(i) 1

(iii) All three × total pressure **(1)**
i.e.

$$pSO_2 = \frac{1.00}{10.5} \times 2.00 \text{ or } {}^{4}\!/_{21}$$
$$= 0.190 \text{ (atm)}$$

$$pO_2 = \frac{0.500}{10.5} \times 2.00 \text{ or } {}^{2}\!/_{21}$$
$$= 0.0952 \text{ (atm)}$$

$$pSO_3 = \frac{9.00}{10.5} \times 2.00 \text{ or } {}^{36}\!/_{21} \text{ or } {}^{12}\!/_{7}$$
$$= 1.71 \text{ (atm)}$$

Mark consequential on (a)(ii) 1

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

K_p = 851 **(1)** atm^{-1} **(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^{-1} dm^3

(b) (i) (K_p) decreases 1

(ii) (K_p decreases so)

Reject any Le Chatelier argument (this prevents access to 1st mark)

fraction/quotient $\dfrac{p^2SO_3}{p^2SO_2 \times pO_2}$

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_{SO_3} decreases whereas p_{SO_2} and p_{O_2} increase) 2

(c) (i) No effect/none/zero (effect) 1

(ii) Increases
OR
more SO_3/more sulphur trioxide
OR
increases amount of SO_3/sulphur trioxide 1

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

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

[13]

31. (a) H^+ 1

Accept H_3O^+

(b) HCOOH/HCO_2H **(1)**
HNO_3 **(1)**
–1 for each extra incorrect answer 2

Accept C and E

[3]

32. (a) (i) pH = 3.5 **(1)**
$\log_{10}[H^+] = -3.5$
$\Rightarrow [H^+] = 3.16 \times 10^{-4}$ (mol dm^{-3}) **(1)**

2.5**(1)** × 10^{-4} (mol dm^{-3}) based on pH = 3.6 (2 marks) 2

Accept T.E. from wrong pH providing < 7

Accept 3.2 × 10^{-4} (mol dm^{-3})

3 × 10^{-4} (mol dm^{-3}) allowed if evidence of rounding being applied

(ii) $K_a = \frac{[H^+][CH_3CH_2CH_2CO_2^-]}{[CH_3CH_2CH_2CO_2H]}$ **(1)** 1

Accept version with $[H_3O^+]$

Accept molecular formulae

Accept $\frac{[H^+][C_4H_7O_2^-]}{[C_4H_8O_2]}$

(iii) $Ka = \frac{[H^+]^2}{[CH_3CH_2CH_2COOH]}$ **(1)**

$= \dfrac{(3.16\times10^{-4})^2}{0.00660}$ (1st mark can be scored here)
$= 1.5 \times 10^{-5}$ (mol dm^{-3}) **(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)

(b) (i) $CH_3CH_2CH_2CO_2H$ ((aq)) + NH_3 ((aq)) →
$CH_3CH_2CH_2CO_2(^-)NH_4(^+)$ ((aq))
Molecular formulae acceptable 1

Accept eqn via $NH_4OH \rightarrow CH_3CH_2CH_2CO_2^- + NH_4^+$

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

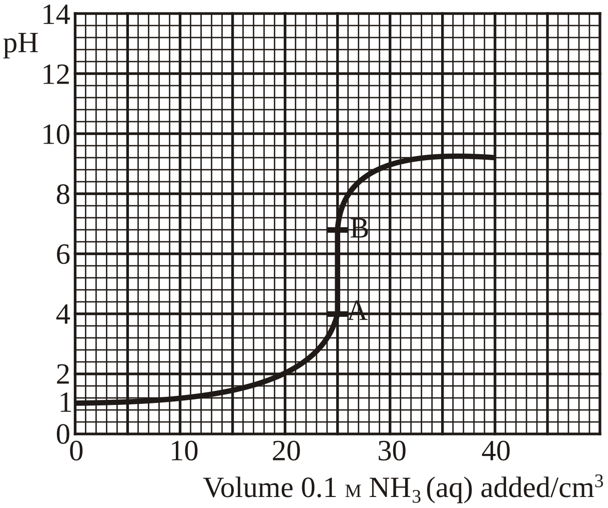
Reject no indicator has the required pH range

(v) EITHER
End-point = 30 cm^3 **(1)**
$\Rightarrow$ [NH_3] = (10/30) × 0.00660 = 0.00220 (mol dm^{-3}) **(1)**
OR
10 cm^3 of butanoic acid contain 6.60×10^{-5} mol
From equation this requires 6.60×10^{-5} mol NH_3
From graph, end-point = 30 cm^3 **(1)**
$\Rightarrow$ [NH_3] = $6.60 \times 10^{-5} \times (1000/30)$
= 2.20×10^{-3} / 0.00220 (mol dm^{-3})**(1)**
Allow internal TE for 2nd mark based on an incorrect equivalence point i.e. 0.0660 (mol dm^{-3}) 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^3 **(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)**

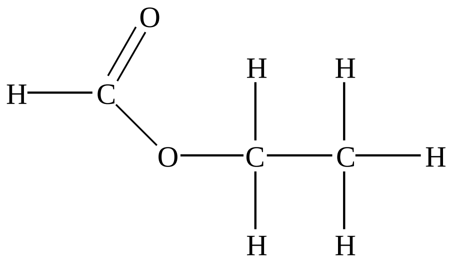
Accept no sharp/clear/precise end point
OR very small range over which indicator changes colour

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_2H_5OH: 3.75 **(1)**

Moles: $HCOOC_2H_5$: 2.50 and moles H_2O : 2.50 **(1) for both** 2

(ii) $K_c = \frac{[HCOOC_2H_5][H_2O]}{[HCOOH][C_2H_5OH]}$ 1

Reject obviously round brackets ***"( )"***

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

Must have clearly divided moles of each component by 0.485 for 1st mark e.g.
$[HCOOC_2H_5] = [H_2O] = 5.16$ (mol dm^{-3})
and $[HCOOH] = 1.03$ (mol dm^{-3})
and $[C_2H_5OH] = 7.73$ (mol dm^{-3})

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

IGNORE sig.figs. 2

Accept $K_c = \dfrac{(2.50)^2}{0.50 \times 3.75}$ *= 3.33 only scores* ***(2)*** *if it is stated that V cancels either here or in (iv)*

If $[H_2O]$ *omitted in (ii), then answer*
$K_c = 0.647\ mol^{-1}\ dm^3$
(2) *but this will give*
$K_c = 1.33\ mol^{-1}\ dm^3$ *with V omitted from calculation* ***(1)***

Reject 1st mark if 485 used as V in expression

(iv) No, (as) equal numbers of moles on both sides
OR volumes cancel
OR mol dm^{-3} 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 $HCOOC_2H_5$ 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) $Ag^+ + I^- \rightarrow AgI$
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).

(initial amount) I^- = 0.100 mol dm^{-3} × 0.050 dm^3 = 5 × 10^{-3} mol **(1)**

Amount Ag^+ = 0.100 mol dm^{-3} × 0.031 dm^3 = 3.1 × 10^{-3} mol **(1)**

∴ equilibrium amount I^- = 3.1 × 10^{-3} mol **(1)**

I^- reacted = (5 – 3.1) × 10^{-3} mol = 1.9 × 10^{-3} mol **(1)**
If this subtraction is not carried out then the next mark (for calculating amount of sulphate) can not be awarded.
Thus amount of sulphate = ½ × 1.9 × 10^{-3} (= 9.5 × 10^{-4} mol) **(1)**

conc iodide = $\dfrac{3.1\times10^{-3}\text{ mol}}{0.05\,\text{dm}^3}$ (= 0.062 mol dm^{-3})

AND conc sulphate = $\dfrac{0.95\times10^{-3}\text{ mol}}{0.05\,\text{dm}^3}$ (= 0.019 mol dm^{-3}) (**1**)
The mark is for the process of dividing by 0.05 dm^3

$K_c = 0.019/0.062^2 = 4.94$ **(1)** Answer must be to 2 or more S.F.
Value consequential on dividing their moles by a volume.

mol^{-1} dm^3 **(1)** Stand alone 8

[10]

36. (a) (i) Pairs: acid NH_4^+ /ammonium ion and base NH_3 /ammonia
acid H_3O^+ / hydronium ion and base H_2O / water 1

Accept hydroxonium ion

(ii) $K_a = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]}$ ignore lower case k 1

Accept $K_a = \dfrac{[NH_3][H^+]}{[NH_4^+]}$

Reject answers including $[H_2O]$

(iii) $[H_3O^+] = 10^{-5}$ mol dm^{-3} **(1)**

Assumption ionization of NH_4^+ (negligibly) small **(1)**

Assumption $[NH_3] = [H_3O^+]$ **(1)**

Accept $[NH_4^+] = [NH_4Cl]$ or NH_4Cl totally ionized

thus $[NH_4Cl] = (1 \times 10^{-5})^2 / 5.62 \times 10^{-10}$
= 0.178 mol dm^{-3} **(1)**
Answer to 2 or more S.F. 4

(iv) QWC

methyl red **(1)**

indicator constant or pK_{In} must be near the endpoint pH
OR indicator constant or pK_{In} must be near 5 **(1)**
2nd mark conditional on correct indicator 2

Accept pK_{In} in the steep part of the graph or it is a weak base-strong acid titration

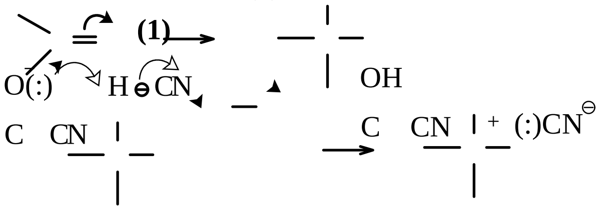
(b) $CN^- + H_2O \rightleftharpoons HCN + OH^-$
IGNORE state symbols 1

Accept "→" instead of "$\rightleftharpoons$"

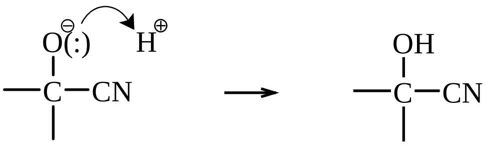
(c) (i) nucleophilic addition 1

(ii)

(1) for both arrows **(1) for intermediate**



OR for second step



(1) 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 ^{-}CN in step 1 (but not from the minus of CN^{-}) and can start from the minus of 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 H^{+}/HCN scores zero
- Autoionisation of C=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 CN^{-}

if too alkaline too little HCN to donate the proton in the last step
OR H^{+} ion concentration too low **(1)** 2

(d) (i) rate = $k[CH_3CH_2CH_2Cl]\,[CN^-]$

Must be an equation

Must be [ ] NOT ( )

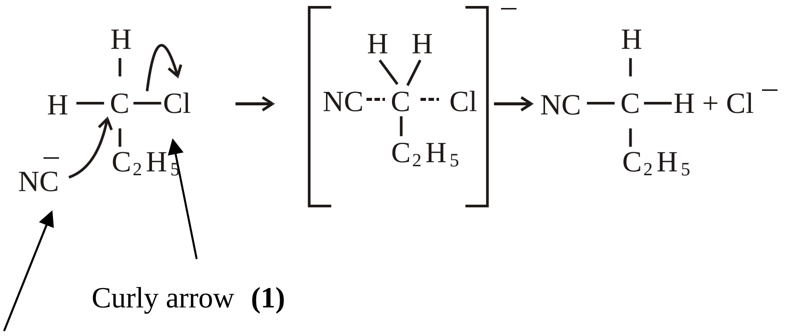
Ignore upper case K 1

Accept 'R' or 'r' for rate $C_3H_7Cl]$ / [1-chloropropane]/ [chloropropane]

Accept [cyanide ion]/[cyanide]

Reject [KCN]

(ii)



Curly arrow **(1)**

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_N1 scores 0

Reject fish hook arrows (penalise once)

Reject arrow from N of CN

[19]

37. (a) (i) [6 × 188.7 + 4 × 210.7] – [4 × 192.3 + 5 × 205] **(1)**

+180.8 J mol^{-1} K^{-1} **(1)**

Accept +181 J mol^{-1} 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 × 1000 /1123 **(1)**

+ 806.4 J mol^{-1} K^{-1} / 0.8064 kJ mol^{-1} K^{-1} **(1)**
[IGNORE SF] 2

Accept + 806 J mol K^{-1}

(iv) +987.2 J mol^{-1} K^{-1} 1

Accept +987 J mol^{-1} K^{-1}
allow TE from (i) & (iii)

No TE if J mol^{-1} K^{-1} *added to kJ* mol^{-1} K^{-1}

(v) All products/reaction goes to completion because $\Delta S_{tot} > 200$ J mol^{-1} K^{-1}/ΔS_{tot} is **very** large
[Needs to be consistent with (iv)] 1

(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) $K_p = \dfrac{pNO_2{}^2}{pNO^2 \times pO_2}$ 1

Accept $\dfrac{p^2 NO_2}{p^2 NO \times pO_2}$

Reject [ ]

(ii) mole fraction $NO_2 = \frac{4.95}{5}$ or 0.99 **(1)**

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

OR

mole fraction $O_2 = \frac{0.025}{5}$ or 0.005 **(1)**

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

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 NO2 increases as eqm moves to side of fewest (gas) molecules/RHS **(1)**
or
Partial pressure of NO2 increases as pp = mole fraction × total pressure 2

Accept justification in terms of entropy

[17]

38. (a) (i) $K_a = \frac{[CH_2ClCO_2^-][H^+]}{[CH_2ClCO_2H]}$ 1

Accept [H_3O^+] in place of [H^+]
allow one set of sq brackets to be missing

(ii) $[H^+]^2 = 1.3 \times 10^{-3} \times 0.001$ **(1)**

$= 1.3 \times 10^{-6}$

$[H^+] = \sqrt{1.3 \times 10^{-6}}$

1.14×10^{-3} **(1)**

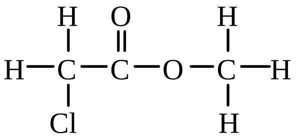
pH $= -\log 1.14 \times 10^{-3} = 2.9(4)$ **(1)**

[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

(b) (i)



$\mathrm{CH_2ClCOOCH_3}$

ester group **(1)**
rest of molecule **(1)** dependent on first mark
(must be fully displayed)
methyl chloroethanoate **(1)** 3

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

2nd and 3rd 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

[15]

39. (a) N/N_2 goes from 0 to –3 = reduction **(1)**
H/H_2 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 × 3 + 944/ (= 2252) **(1)**
Calculation of bonds made 388×6/ (= 2328) **(1)**
$\Delta H = -76$ (kJ mol^{-1}) **(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 ΔH 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^{-1})

(c) (i) QWC

<u>One way</u>

temperature increase therefore molecules have greater (average kinetic) energy **(1)**

Accept moving faster

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

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

Accept $E > E_{act}$ *particles for molecules*
greater frequency of successful collisions/ more successful conditions per unit time

Reject just "more successful collisions"

<u>Another way</u>

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 $E \geq E_{cat}$/ 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 ΔH *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

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

If [HI] not squared, first mark only.

Second mark:

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

OR

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

OR

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

Third mark:

$[\mathrm{HI}_{(g)}] = 3.6 \times 10^{-3}$ (mol dm^{-3}) **(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^{st} mark is for calculating equilibrium moles

H_2 = 0.2

I_2 = 0.2

HI = 1.6 **(1)**

Mark consequentially

2^{nd} mark is for dividing these by 2 (to get mole fractions)

$$x_{H2} = \frac{0.2}{2.0} = 0.1$$

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

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

Mark consequentially

3^{rd} mark is for multiplying by 1.1 (to get partial pressures)

$$\mathrm{P}_{H_2} = \frac{0.2}{2.0} \times 1.1$$

= 0.11 (atm)

$$\mathrm{P}_{I_2} = \frac{0.2}{2.0} \times 11$$

= 0.11 (atm)

$$\mathrm{P}_{HI} = \frac{1.6}{2.0} \times 11$$

= 0.88 (atm) **(1)**

Mark consequentially

4^{th} mark is for substituting into their expression and calculating K_p

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

= 64 **(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^{-3} cancel'

[11]

41. (a) (i) One acid: $CH_3CH_2COOH(aq)$
Conjugate base: $CH_3CH_2COO^-(aq)$ **(1)**

Other acid: $H_3O^+(aq)$
Conjugate base: $H_2O(l)$ **(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_3O^+ / hydrogen / H^+ ions

Reject just "contains H_3O^+ …."

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

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

Reject any expression containing $[H_2O]$

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

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

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

Or

$$[CH_3CH_2COOH] = \frac{(3.63 \times 10^{-4})^2}{1.30 \times 10^{-5}} \textbf{ (1)}$$

= 0.010 **(1)** (mol dm^{-3}) **(1)**

<u>ASSUMPTIONS</u>:

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 $[H^+]<<[HA]$ **(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:

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

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.

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

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

pH = 5.06 **(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:

$pH = pK_a - \log_{10}\frac{[\text{acid}]}{[\text{salt}]}$ **(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.

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

= 4.89 – (–0.18)

= 5.07 **(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) $(p_{NO})^2 = 0.87 \times 0.23 \times 5.0 \times 10^{-31}$ **(1)**
$= 1.0 \times 10^{-31}$

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

Accept 3.16×10^{-16} *(atm)* ***(1)***

Ignore sig fig

Mark consequentially only if based on reciprocal of
correct expression in (a)(i) 2

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

Allow TE from (b)(i) 1

Reject answer based on adding ***2 ×*** *p_{NO}*

(iii) p_{NO} doubles/will become 6.4×10^{-16} atm **(1)**

K_p remains constant/is (still) 5.0×10^{-31} **(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_2 and O_2 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) (ΔH is positive so) $-\frac{\Delta H}{T} = \Delta S_{surroundings}$ 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) $\Delta S_{surroundings}$ becomes greater/less negative/ more positive, so ΔS_{total} (also) becomes greater/less negative/more positive/increases 1

Accept $\Delta S_{surroundings}$ becomes "smaller", <u>if qualified</u>, 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_2 and O_2)

Accept temperature inside engine may be <u>less</u> than 1500K

Accept actual (total) pressure may be less than that assumed

[12]

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

Accept $pK_a = 4.20$ ***(1)***

Both correct **(1)**

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

$[H^+]$ (= $K_a \times [C_6H_5CO_2H] / [C_6H_5CO_2^-]$
= $6.3 \times 10^{-5} \times 0.0020 / 0.016$)
= 7.875×10^{-6} **(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 **(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 $^{[acid]}/_{[base]}$ *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) $K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$

IGNORE UNITS HERE 1

Reject [ ]

(b) (i) p_{NO_2} = 0.8 × 1.1
= 0.88 (atm)

and

$p_{N_2O_2}$ = 0.2 × 1.1
= 0.22 (atm) **(1)**

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

K_p = 3.52 **(1)**
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 **(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.

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

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

P_T = 0.435 (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/ $\frac{p^2_{NO_2}}{p_{N_2O_4}}$ /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]

45. (a) (i) $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

OR

$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

IGNORE STATE SYMBOLS 1

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

(ii) $K_W = [H^+_{(aq)}][OH^-_{(aq)}]$

OR

$K_W = [H_3O^+_{(aq)}][OH^-_{(aq)}]$

IGNORE STATE SYMBOLS 1

*If $[H_2O]$ included **(0).***

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

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

OR

$pH = -\log_{10}[H_3O^+]$

OR

in words 1

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

(iv) $K_W = [H^+][OH^-]$
$5.48 \times 10^{-14} = [H^+]^2$ **(1)**
$[H^+] = \sqrt{5.48 \times 10^{-14}}$
$[H^+] = 2.34 \times 10^{-7}$ (mol dm^{-3})
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_2O]
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 = antilog$_{10}$(–4.8)
$K_a = 1.6 \times 10^{-5}$ (mol dm^{-3}) **(1)**

Mark CQ on pKa
Accept if pKa = 4.9, Ka = 1.3 × 10^{-5}

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^{-9} 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 (J mol^{-1} K^{-1})

"+" sign essential 1

Accept +(0).2156 kJ mol^{-1} K^{-1}
OR +0.216 kJ mol^{-1} K^{-1}

Reject 215 J mol^{-1} K^{-1}
Reject 0.215 kJ mol^{-1} 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 2nd mark

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

OR
$\dfrac{-123800}{298}$ **(1)**

$= -415\ \text{J mol}^{-1}\ \text{K}^{-1}$ **(1)** 2

Accept – 0.415 kJ mol^{-1} K^{-1}

Accept –415.4 J mol^{-1} 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) (J mol^{-1} K^{-1})
IGNORE 4th significant figure 1

Accept –0.199 kJ mol^{-1} 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) $K_p = \dfrac{p_{PCl_3} \times p_{CL_2}}{p_{PCl_5}}$ **(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 atm^{-1}

Reject use of [ ]

(ii)

Substance	Moles at start	Moles at equilibrium	P_{eq} /atm
$PCl_5(g)$	**0.20** **(1)**		$\frac{\mathbf{0.15}}{\mathbf{0.25}} \times \mathbf{4.32}$ **= 2.592**
$PCl_3(g)$		**0.05**	$\frac{\mathbf{0.05}}{\mathbf{0.25}} \times \mathbf{4.32}$ **= 0.864**
$Cl_2(g)$		**0.05**	**0.864**
Total number of moles at equilibrium		**0.25**	

All three**(1)** All three**(1)**

Allow consequential marking across columns 3

If moles at eqm are given as 0.025 for $PCl_3(g)$ *and for* $Cl_2(g)$ *then 4th 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 (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) $K_a = \frac{[H^+][HCO_3^-]}{[CO_2]}$ **(1)**

mol dm^{-3} **(1)**

If H_2O is included as denominator then allow only the 2nd mark if no units suggested 2

(ii) pKa = – log Ka / – lg Ka / – $\log_{10} K_a$ 1

Accept $K_a = 10^{-pKa}$

(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 $H_2CO_3/CO_2 + H_2O$) 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

$[CO_2] = 0.126 \times 0.0224 = 2.82 \times 10^{-3}$

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 $[CO_2]$ / $[HCO_3^-]$ / $[CO_2 + HCO_3^-]$
OR
Hypothesis II would produce greater acidity without additional $[CO_2]$ / $[HCO_3^-]$ / $[CO_2 + HCO_3^-]$ **(1)**

The table shows a fall in $[CO_2]$ / $[HCO_3^-]$ / $[CO_2 + HCO_3^-]$ 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

[3]

54. (a) methyl butanoate
Accept Methyl butaneoate 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) Kc = $\frac{[C_3H_7COOH(l)][CH_3OH(l)]}{[C_3H_7COOCH_3(l)][H_2O(l)]}$ **(1)**

Accept eq subscripts

	Moles at equilibrium	Concentration / mol dm^{-3}
butanoic acid = 4.4/88 =	0.05	1.67
methanol	0.05	1.67
ester (methyl butanoate)	0.05	1.67
water	0.95	31.7

all four equilibrium moles = **(1)**
Conc at equilibrium = equilibrium moles ÷ 0.030 **(1)**

Kc = $\frac{1.67 \times 1.67}{1.67 \times 31.7}$ **(1)** = 0.053 **(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 × 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 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 × 0.1/24 J = 1 946 J
20 × 4.18 × ΔT = 1 946 **(1)**
$\Delta T = 23.3^{(o)}$ **(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/time = 0.25 s^{-1} ln(rate) = –1.39 **(1)**

At 283 time 124s 1/time = 0.00806 s^{-1} ln(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 × 8.31
= + 58.2 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 ≥ 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]