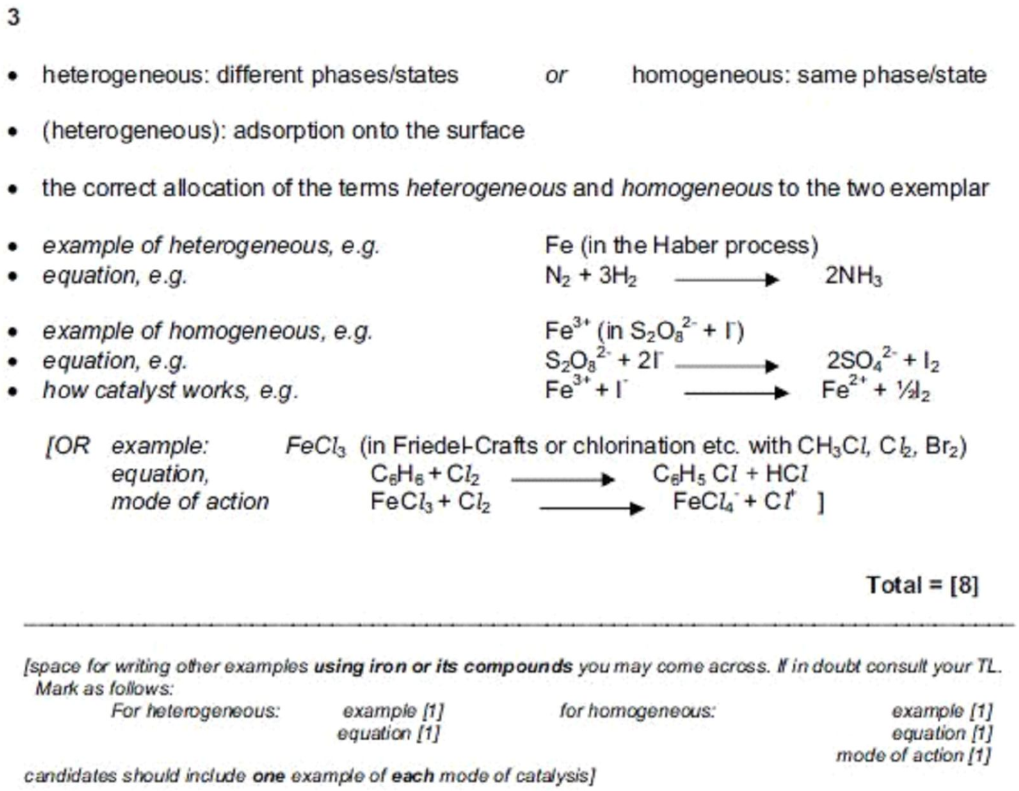
Q1.



3

- heterogeneous: different phases/states *or* homogeneous: same phase/state
- (heterogeneous): adsorption onto the surface
- the correct allocation of the terms *heterogeneous* and *homogeneous* to the two exemplar

- *example of heterogeneous, e.g.* Fe (in the Haber process)
- *equation, e.g.* $N_2 + 3H_2 \longrightarrow 2NH_3$

- *example of homogeneous, e.g.* Fe^{3+} (in $S_2O_8^{2-} + I^-$)
- *equation, e.g.* $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$
- *how catalyst works, e.g.* $Fe^{3+} + I^- \longrightarrow Fe^{2+} + \frac{1}{2}I_2$

[OR example: *FeCl*$_3$ (in Friedel-Crafts or chlorination etc. with CH_3Cl, Cl_2, Br_2)
equation, $C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$
mode of action $FeCl_3 + Cl_2 \longrightarrow FeCl_4^- + Cl^+$]

Total = [8]

[space for writing other examples ***using iron or its compounds*** *you may come across. If in doubt consult your TL.*
Mark as follows:
For heterogeneous: *example [1]* *for homogeneous:* *example [1]*
equation [1] *equation [1]*
mode of action [1]
candidates should include ***one*** *example of* ***each*** *mode of catalysis]*

Q2.

2 **(a)** The **power/index/exponent** to which a **concentration** term is raised in a **rate equation**

or ^{a} in rate = **k**$[A]^a$ (k is needed – or can use rate $\alpha [A]^a$) **[1]**

Part (a): [1]

(b) **(i)** 1st order w.r.t. propanone **[1]**

Zero order w.r.t. H^+ ions **[1]**

1st order w.r.t. CN^- ions **[1]**

(ii) Rate = k [propanone]$[CN^-]$ (e.c.f. from **(i)**) **[1]**

(iii) Mechanism **B** (**or A** – see grid below), with the first (**or** second – see grid below) step being the slow step, **[1]**

(since H^+ does not appear in rate equation) it must be involved **after** the slow step **or** $[H^+]$ is not involved in slow step **[1]**

Grid for e.c.f. in first mark of **(iii)**

Deductions in (i) or (ii)			**E.C.F. deductions in (iii)**	
[Propanone]	$[CN^-]$	$[H^+]$	Mechanism	Slow step
1	1	0	B	1st
1	0	1	A	1st
1	1	1	A **or** B	2nd
Any other			No e.c.f. mark can be awarded	

Part (b): [6]

Total: [7]

Q3.

1 **(a)** **(i)** order w.r.t. NO = 2 [1]
order w.r.t. O_2 = 1 [1]

(ii) rate = $k[NO]^2[O_2]$ [1]

taking the first row: $k = \text{rate}/([NO]^2[O_2])$
$= 0.020/(0.005^2 \times 0.005)$
$= \mathbf{1.6 \times 10^5}$ ecf [1]
units = $\mathbf{mol^{-2}dm^6sec^{-1}}$ ecf [1]

(iii) rate $= k[NO]^2[O_2]$
$= 1.6 \times 10^5 \times 0.0025^2 \times 0.0025$
$= \mathbf{2.5 \times 10^{-3}}$ ($mol\ dm^{-3}\ s^{-1}$) ecf [1]

[6]

(b) **(i)** homogeneous [1]

(ii) $NO + \frac{1}{2}O_2 \longrightarrow NO_2$
$SO_2 + NO_2 \longrightarrow SO_3 + NO$
($SO_3 + H_2O \longrightarrow H_2SO_4$) [2]

[3]

[Total: 9]

Q4.

(d) **(i)**

- instrumental method (e.g. spectrophotometer/colorimeter/conductance meter)
- what is measured (e.g. absorbance/transmission at a **stated** wavelength *or* by use of a "suitable" (green) filter *or* conductance/resistance)
- measurement of time
- relation of time to rate (e.g. gradient of absorbance/time graph, *or* rate ∝ 1/t)
- repeat with different [Zn^{2+}], (but the same [PAR])
- relation of rate to [Zn^{2+}] (either by a plot or by simple proportion)

(all 6 points are unconditional on each other) any 5 points **[5]**

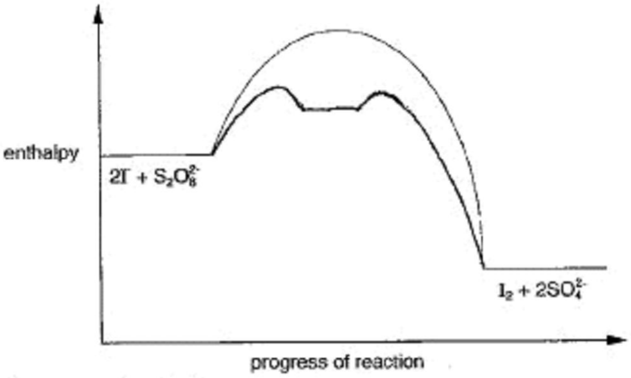
(ii) e.g. add Br_2(aq) [1]
decolourises *or* produces a white ppt. [1]
or add $FeCl_3$(aq or "neutral"); purple colour produced *[1] + [1]* **[2]**

Q5.

4 **(a)** **(i)** homogeneous [1]

(ii) ions in **2** and **3** are oppositely charged ions (thus attract each other) *or* ions in **1** are similarly charged ions (thus repel each other) [1]

(iii)



two contiguous activation humps [1]
both less than the original [1]
starting and finishing at the same points as before [1] **[5]**

(b) **(i)** SO_3 produces acid rain *or* $SO_3 + H_2O \longrightarrow H_2SO_4$ *or* a consequence of acid rain, e.g. lower pH of lakes; leaches aluminium from soils; kills fish/plants/rainforests; dissolves/corrodes/damages buildings (NOT global warming) [1]
(NOT asthma etc – since this is not environmental)

(ii) the burning of fossil fuels/coal/oil/petrol/gas/diesel/fuel *or* car exhausts *or* roasting of sulphide ores *or* cement manufacture *or* volcanoes [1]

(iii) $SO_2 + NO_2 \longrightarrow SO_3 + NO$ [1]

$NO + \frac{1}{2}O_2 \longrightarrow NO_2$ [1]
[4]

[Total: 9]

Q6.

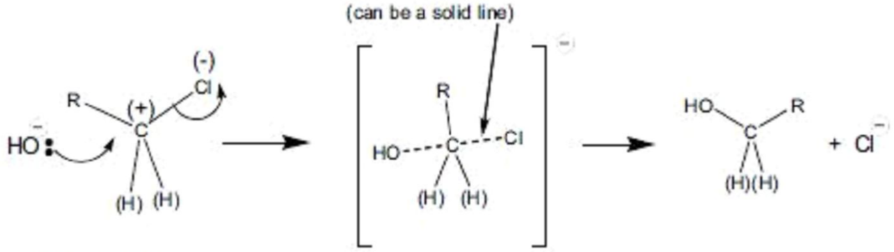
1 **(a)** C_6H_5-$COCH_2OH$ *or* $C_8H_8O_2$ **and** NaC*l* *or* C*l*$^-$ (1) + (1) [2]

(b) **(i)** the exponent / power to which a concentration is raised in the **rate equation** (or in an equation, e.g. "a" in the equ: rate = $k[A]^a$) (1)

(ii) from 1 and 2: rate increases by 50% as does [RC*l*], so rate $\propto$ $[RCl]^1$ (1)
from 1 and 3: rate $\propto$ $[NaOH]^1$ (1)

(iii) (rate =) $k[RCl][OH^-]$ (1)

(iv)



marking points:

- (+) or $^{\delta+}$ on C **and** (–) or $^{\delta-}$ on C*l* (1)
- lone pair **and** charge on: OH^- (1)
- curly arrow from OH (lone pair) to $^{(\delta+)}$C, **and** *either* a curly arrow breaking C-C*l* bond *or* 5-valent transition state (ignore charge) (1)
- S_N1 alternative for last mark (only award mark if candidate's rate equation shows first order reaction): curly arrow breaking C-C*l* bond **and** carbocation intermediate. [7]

(c) **(i)** (add RC*l* / RCOC*l* to) (aq) Ag^+ / $AgNO_3$ *or* named indicator (e.g. MeOr) *or* use pH probe (1)

White ppt appears (faster with RCOC*l*) *or* turns acidic colour (e.g. red) *or* shows pH decrease (1)

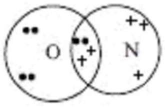
if water is the only reagent, and no pH meter used: award only the second mark, for "steamy / white fumes"

(ii) (C=O is polarised /) carbon is more $\delta+$ than in R-C*l* *or* carbon is positive *or* RCOC*l* can react via addition-elimination
(mention of electronegativity on its own is not enough for the mark) (1) [3]

[Total: 12]

Q7.

2. **(a)** **(i)**



[1]

(ii) -180 kJ mol^{-1} [1]

(iii) (formation of NO is endothermic) so high T **and** equilibrium pushed over to NO side.
or high T **and** needed to break N-N bond in N_2 [1]

(iv) $-180 = 2\,E(NO) - 994 - 496$ [1]
E(NO) = **+655 kJ mol^{-1}** [1]
[5]

(b) **(i)** (from 1 and 2:) as p(NO) halves, rate decreases to ¼ , **so order = 2** [1]
(from 1 and 3:) as p(H_2) halves, so does rate, **so order = 1** [1]

(ii) rate = $k\, p_{NO}^{2}.p_{H2}$ [1]
units (of k) are atm^{-2} s^{-1} [1]

(iii) add all three equations:
$NO + NO + H_2 + O + H_2 + N_2O \rightarrow N_2O + O + H_2O + N_2 + H_2O$ [1]
cross out all species common to both sides:
$NO + NO + H_2 + \cancel{O} + H_2 + \cancel{N_2O} \rightarrow \cancel{N_2O} + \cancel{O} + H_2O + N_2 + H_2O$ [1]
$(\Rightarrow \quad 2NO + 2H_2 \rightarrow N_2 + 2H_2O)$

(iv) *either*: **step 2** since it involves H_2 [1]
O formed from NO [1]
or: ***step 3*** *since it involves* H_2 *[1]*
N_2O *formed from NO* *[1]*
[8]

(c) **(i)** NO [1]

(ii) $3Fe^{2+} + 4H^{+} + NO_3^{-} \longrightarrow 3Fe^{3+} + NO + 2H_2O$ [1]
(allow $Fe^{2+} + H^{+} + HNO_2 \longrightarrow Fe^{3+} + NO + H_2O$)

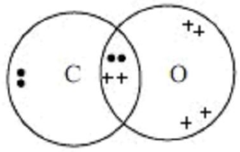
(iii) dative/coordinate bonding [1]

(iv) $[Fe(H_2O)_{6-n}(NO)_n]^{2+}$ (n = 1-6) [1]
[4]

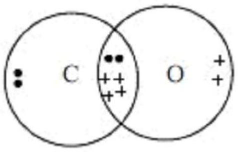
[Total:17]

Q8.

2 **(a)** **(i)**



or



[1]

(ii) incomplete combustion (of hydrocarbon fuels) *or* insufficient O_2/air [1]

(iii) $NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$
or $CO + \frac{1}{2}O_2 \rightarrow CO_2$
equation needs to be balanced [1]
[3]

(b) $\Delta H = 394 - 2 \times 111 = (+)172$ kJ mol^{-1} [2]
[2]

(c) **(i)** ligand exchange/displacement/replacement/substitution [1]

(ii)

- d-orbitals are split (by the ligand field) *or* orbitals near ligands are at higher energy
- the splitting/energy gap depends on the ligands (surrounding the ion) *or* the metal (ion)
- when <u>an electron</u> moves from lower to higher orbital/energy level *or* is promoted/excited
- light/a photon is absorbed *or* colour seen/reflected/transmitted is complement of colour absorbed ("emitted" contradicts this mark)
- different energy gap means different frequency absorbed means different colour

5 × [1]

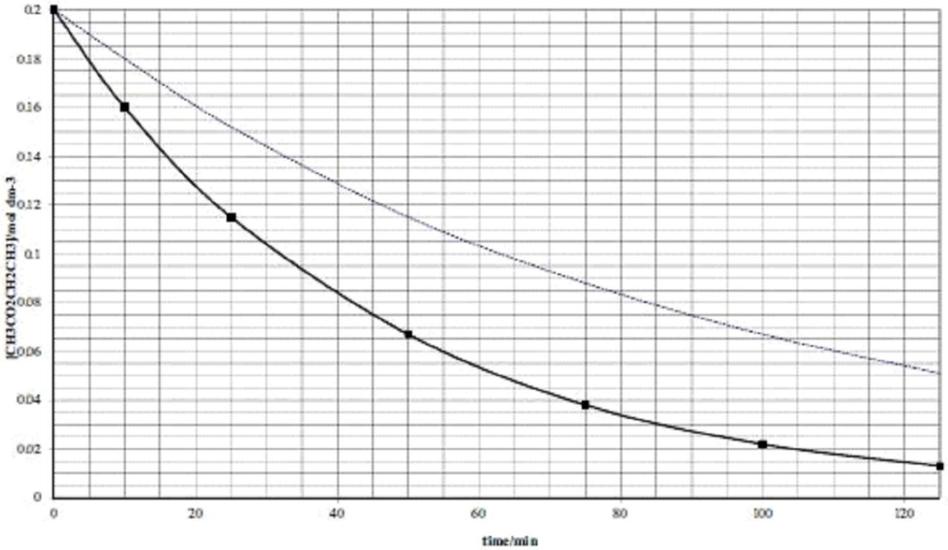
(iii) from rows 1 and 3: rate3/rate1 = 2.0 which also equals $[[complex]_3]/[[complex]_1]$ [1]
(*or* this working mark can be awarded for any valid calculation that shows that order w.r.t. complex is 1)
Thus order w.r.t. [complex] = 1 **and** order w.r.t. [CO] is zero [1]
rate equation: **rate = k[complex]** [1]

(iv) mechanism 2 [1]
it's the only one that does **not** involve CO in the rate determining step *or* rate depends on [complex] <u>only</u>. [1]
[11 max 10]

[Total: 15]

Q9.

2 (a) (i)



plotting of points (–1 for any error – plotted to within ½ square) [1]
a good best fit curve [1]

(ii) construction lines for two half-lives **and** $t_{½} \approx 63$ m or 32 m (±3 min) / $t_{½}$ is constant
or
construction lines for two tangents **and** mention of two values / concentration doubled, rate doubled [1]

(iii) *either* ratio of (initial) rates (slopes) *or* ratio of $t_{½} = 2.0$ [1]

so reaction is first order w.r.t. [HC*l*] [1]

(iv) rate = k[$CH_3CO_2CH_2CH_3$][HC*l*] conditional on **(a)(iii) and** ecf from **(a)(iii)** [1]

(initial) rate = 0.2/95 *or* 0.2/47
$\approx 2.1 \times 10^{-3}$ *or* 4.3×10^{-3} (mol dm^{-3} min^{-1}) [1]

k = $2.1 \times 10^{-3} / (0.2 \times 0.1)$ *or* $4.3 \times 10^{-3} / (0.2 \times 0.2)$
≈ 0.11 (mol^{-1} dm^3 min^{-1}) [1]
[8 max 7]

(b) (i) because H_2O is the solvent *or* its concentration cannot change [1]

(ii) because HC*l* is a catalyst [1]
[2]

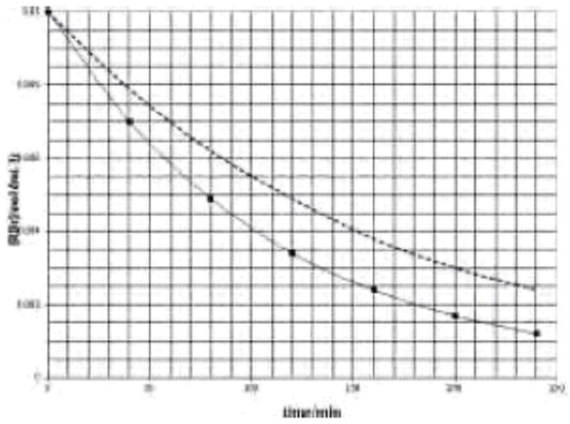
[Total: 9]

Q10.

1 **(a)** **(i)** RBr + OH^- $\longrightarrow$ ROH+ Br^- [1]

(ii) nucleophilic substitution [1]
[2]

(b) **(i)**



plotting of all points (plotted to within ½ small square) [1]
good line of best fit [1]

(ii) $t_{½}$ = 118 min or 79 min (± 5 min)
or
construction lines for two half-lives **and** mention that half-life is constant
or
calculate the ratio of two rates at two different concentrations [1]

(iii) either ratio of initial rates (slopes)
or
ratio of $t_{½}$
or
ratio of times for [RBr] to fall to the same level: all should be = 1.5 [1]

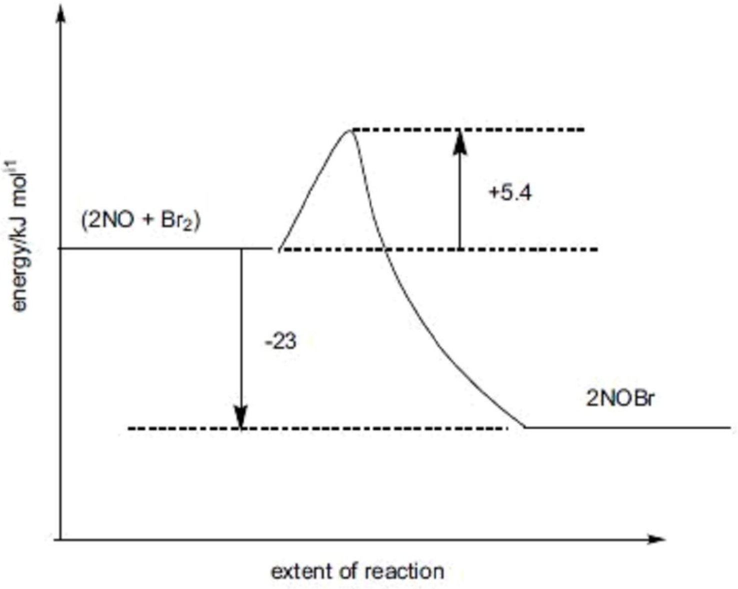
therefore reaction is first order w.r.t. [OH^-] [1]

(iv) rate = k[RBr][OH^-] [1]

initial rate = 0.01 / 185 = 5.4×10^{-5} (mol dm^{-3} min^{-1}) [1]

k = 5.4×10^{-5} / (0.01 × 0.1) = 0.054 (mol^{-1} dm^3 min^{-1}) [1]
[8 max 7]

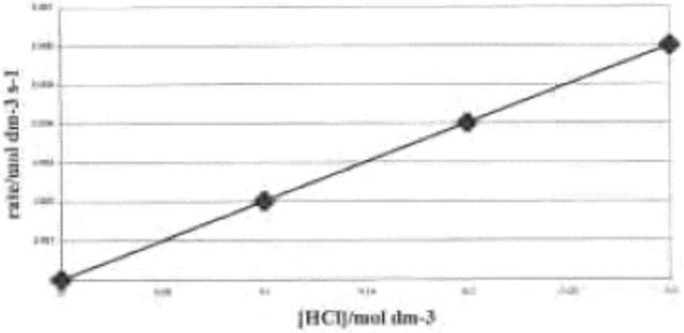
(c)



four marking points: one activation "hump"
2NOBr (not just NOBr)
ΔH labelled correctly (arrow down, or double headed, or just a line)
E_a labelled correctly (arrow up, or double headed, or just a line)
all four points [2]
three or two points [1]
[2]

[Total: 11]

Q11.

1	**(a)**		The power to which the **concentration** (of reagent) is raised (in the rate equation) *or*: the value of *a* in the expression rate = $k[A]^a$	(1)	**[1]**
	(b)		rate = $k[CH_3COCH_3][H^+]$	(1)	**[1]**
	(c)	**(i)**	A	(1)	
		(ii)	B	(1)	**[2]**
	(d)		 line (through zero) clear points	(1) (1)	**[2]**
	(e)		mechanism B	(1)	
			because the rate is determined by the slow step, which involves propanone + H^+, but not I_2 — any two points	(2)	**[3]**
	(f)	**(i)**	titration with thiosulphate *or* colorimetry	(1)	
		(ii)	$k = \text{rate}/[\text{propanone}][H^+] = 3.3 \times 10^{-6}/(0.2 \times 0.5) = 3.3 \times 10^{-5}$	(1)	
		(iii)	units are $mol^{-1}\ dm^3 s^{-1}$	(1)	**[3]**
					Total: 12

Q12.

2 **(a)** solution will turn brown/purple [1]

(b) table:

case	*a*	*b*	*c*
1	1	1	0
2	1	1	1
3	1	2	2

each horizontal row scores [1]
if no marks scored, a correct vertical row can score [1] [3 max]

(c) rate = $6.5–7.5 \times 10^{-6}$ [1]
units are mol dm^{-3} s^{-1} [1]

(d) half-life measured and quoted as ≅ 90–94 s [1]
evidence of two half-lives measured [1]

(e) lines 1 and 2: as $[H_2O_2]$ increases by 0.07/0.05 = 1.4, so does rate
so order w.r.t. $[H_2O_2]$ = **1** [1]
lines 1 and 3: increase in rate (1.8) is also the increase in $[H_2O_2]$,
so rate is **independent** of $[H^+]$ (*or* zero order) [1]

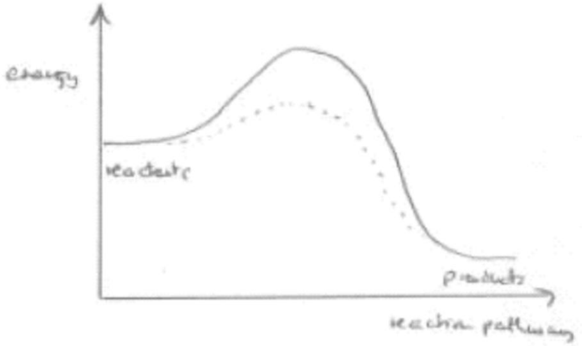
a description can be accepted here
if both orders are correct but no working/explanation given score [1]

(f) the first step/or the relevant equation [1]

[Total: 11]

Q13.

8 **(a)** **(i)**



dotted line must start and end at same points [1]

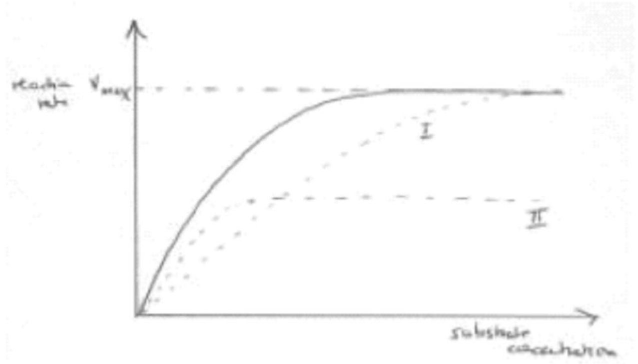
(ii) protein/polypeptide NOT polymer/polyamide [1]

(iii) they are denatured/lose their 2°/3° structure/or H-bonds/vdW [1]

(b) **(i)** competitive inhibitor resembles the substrate OR competes for the active site of the enzyme [1]

non-competitive inhibitor can bind to a different site on the enzyme OR forms a covalent bond/bonds permanently with the enzyme [1]

(ii)



mark for each line NB lines must cross to score mark for **II** [2 × 1]

(c) **(i)** –S–H groups (allow sulphide/S/cysteine residue) [1]

(ii) this inhibits/reduces/decreases the enzyme activity/stops normal function [1]
the bonding disrupts the 3-dimensional structure of the enzyme [1]

[Total: 10]

Q14.

3 **(a)** Any two from:
high(-ish) density of metal
variable oxidation states
ability to form complexes
formation of coloured compounds
incomplete d subshell
high m.p. / b.p. [1] + [1]
[2]

(b) equ: $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ [1]

method:
Take a known volume of Fe^{2+}(aq)/in a pipette and place in (conical) flask
Add an excess of (dil) H_2SO_4
Titrate until end point is reached and note volume used
End point is first permanent pink colour
Repeat titration & take average of consistent readings
any 3 points [3]
[4]

(c) **(i)** $\mathbf{2}\,MnO_4^- + \mathbf{5}\,SO_2 + \mathbf{2}\,H_2O \rightarrow \mathbf{2}\,Mn^{2+} + \mathbf{5}\,SO_4^{2-} + \mathbf{4}\,H^+$ [2]

oxidation numbers: **+7** **+4** **+2** **+6** [1]

(ii) $\mathbf{1}\,Cr_2O_7^{2-} + \mathbf{6}\,NO_2 + \mathbf{2}\,H^+ \rightarrow \mathbf{2}\,Cr^{3+} + \mathbf{6}\,NO_3^- + \mathbf{1}\,H_2O$ [2]

oxidation numbers: **+6** **+4** **+3** **+5** [1]

([2] marks for each equation: [1] for balancing of redox species,
[1] for total balancing: i.e. H_2O and H^+)
[6]

(d) Fe^{3+} is a homogeneous (catalyst)
Fe^{3+} oxidised I^- (and is reduced to Fe^{2+})
Fe^{2+} reduces $S_2O_8^{2-}$ (and is oxidised to Fe^{3+})
or equations showing this any two points [2]
[2]

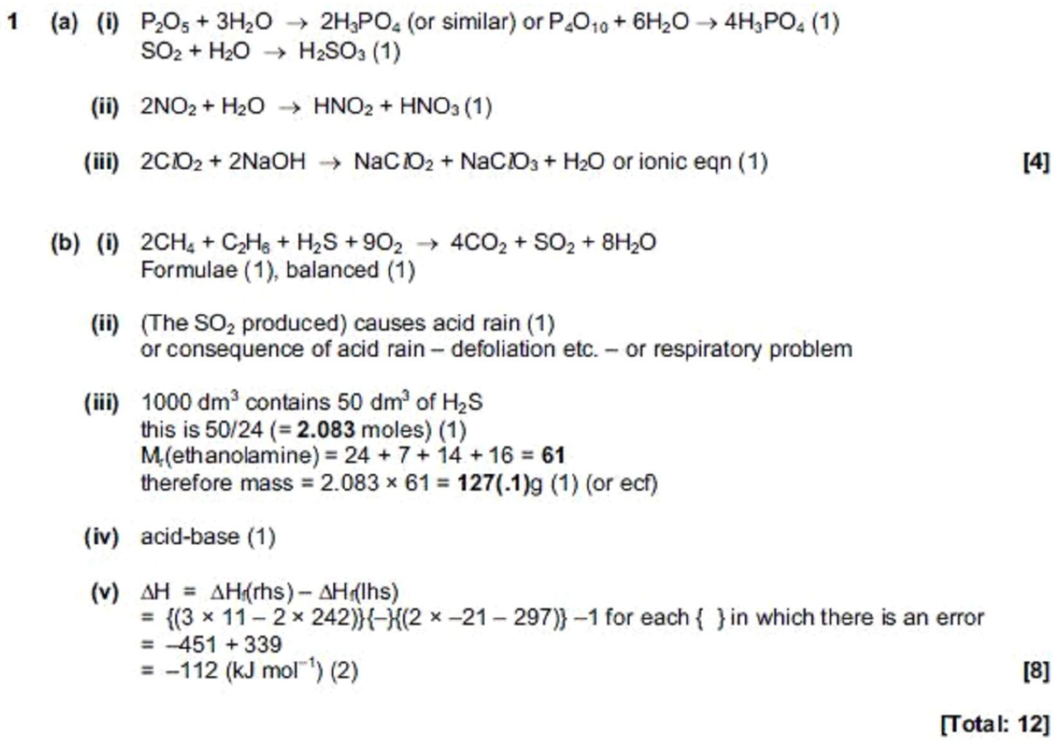
[Total: 14]

Q15.

(b) Substrate binds to the active site of the enzyme [1]
Interaction with site causes a specific bond to be weakened, (which breaks)
Or change in shape weakens bond(s) / lowers activation energy [1]
[2]

(c) Non-competitive inhibition [1]
Rate never reaches V_{max} [1]
[2]

Q16.



1 **(a)** **(i)** $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$ (or similar) or $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ (1)
$SO_2 + H_2O \rightarrow H_2SO_3$ (1)

(ii) $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$ (1)

(iii) $2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$ or ionic eqn (1) **[4]**

(b) **(i)** $2CH_4 + C_2H_6 + H_2S + 9O_2 \rightarrow 4CO_2 + SO_2 + 8H_2O$
Formulae (1), balanced (1)

(ii) (The SO_2 produced) causes acid rain (1)
or consequence of acid rain – defoliation etc. – or respiratory problem

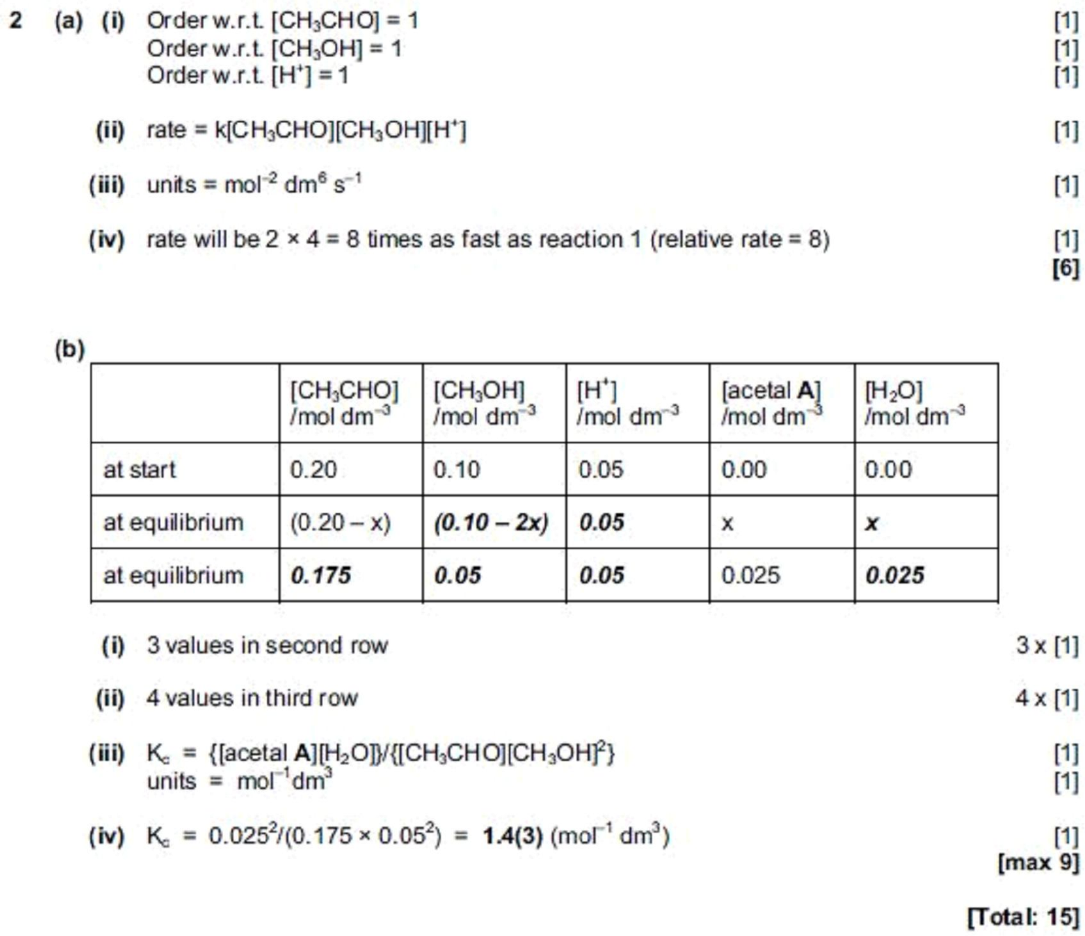
(iii) 1000 dm^3 contains 50 dm^3 of H_2S
this is 50/24 (= **2.083** moles) (1)
M_r(ethanolamine) = 24 + 7 + 14 + 16 = **61**
therefore mass = 2.083 × 61 = **127(.1)**g (1) (or ecf)

(iv) acid-base (1)

(v) $\Delta H = \Delta H_f(\text{rhs}) - \Delta H_f(\text{lhs})$
$= \{(3 \times 11 - 2 \times 242)\}\{-\}\{(2 \times -21 - 297)\}$ –1 for each { } in which there is an error
$= -451 + 339$
$= -112$ ($kJ\ mol^{-1}$) (2) **[8]**

[Total: 12]

Q17.



2 **(a)** **(i)** Order w.r.t. $[CH_3CHO] = 1$ [1]
Order w.r.t. $[CH_3OH] = 1$ [1]
Order w.r.t. $[H^+] = 1$ [1]

(ii) rate = $k[CH_3CHO][CH_3OH][H^+]$ [1]

(iii) units = $mol^{-2}\ dm^6\ s^{-1}$ [1]

(iv) rate will be 2 × 4 = 8 times as fast as reaction 1 (relative rate = 8) [1]
[6]

(b)

	$[CH_3CHO]$ /mol dm^{-3}	$[CH_3OH]$ /mol dm^{-3}	$[H^+]$ /mol dm^{-3}	[acetal **A**] /mol dm^{-3}	$[H_2O]$ /mol dm^{-3}
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20 – x)	***(0.10 – 2x)***	***0.05***	x	***x***
at equilibrium	***0.175***	***0.05***	***0.05***	0.025	***0.025***

(i) 3 values in second row 3 x [1]

(ii) 4 values in third row 4 x [1]

(iii) $K_c = \{[\text{acetal } \mathbf{A}][H_2O]\}/\{[CH_3CHO][CH_3OH]^2\}$ [1]
units = $mol^{-1} dm^3$ [1]

(iv) $K_c = 0.025^2/(0.175 \times 0.05^2) =$ **1.4(3)** ($mol^{-1}\ dm^3$) [1]
[max 9]

[Total: 15]

Q18.

2 **(a)** **(i)** A molecule/ion/species with a lone pair (of electrons) *or* electron pair donor...
.... that bonds to a metal ion/transition element.... [1]

(ii) ...by means of a dative/coordinate (covalent) bond [1]
[2]

(b) **(i)** straight line from (0, 0.01) to point at (350, 0.0028) with all points on the line [1]

(ii) order w.r.t. $Cr(CO)_6$ is 1 **and** order w.r.t. PR_3 is zero [1]
because **(a)** $Cr(CO)_6$ graph has a constant half-life (which is 700 s)
or construction lines on graph showing this) [1]
because **(b)** PR_3 graph is a straight line (of constant slope) *or* line shows a constant rate of reaction *or* no change in rate *or* shows a linear decrease [1]

(iii) rate = $k[Cr(CO)_6]$ [1]

k = (**0.9 – 1.1**) **× 10^{-3}** (s^{-1}) (one or more s.f.) [1]

either $rate_0 = 0.01/1020 = 9.8 \times 10^{-6}$ mol sec^{-1} when $[Cr(CO)_6] = 0.01$ mol dm^{-3}
so $k = 9.8 \times 10^{-6}/0.01 = \mathbf{9.8 \times 10^{-4}}$
or $t_{1/2} \approx 700$ sec
$k = 0.693/700 = \mathbf{9.9 \times 10^{-4}}$

(iv) (units of k are) **sec^{-1}** [1]

(v) N.B. the chosen mechanism must be consistent with the rate equation in **(iii)**. Thus:
either if rate = $k[Cr(CO)_6]$
mechanism **B** is consistent [1]
because it's the only mechanism that does NOT involve PR_3 in its slow/rate-determining step *or* only $Cr(CO)_6$ is involved in slow step *or* $[PR_3]$ does not affect the rate [1]

or

if rate = $k[Cr(CO)_6][PR_3]$, then
mechanism **A** or **C** or **D** is consistent [1]
because both reactants are involved in slow step [1]
[9]

[Total: 11]

Q19.

3 **(a)** **(i)** heterogeneous: different states **AND** homogeneous: same state [1]

(ii) the correct allocation of the terms *heterogeneous* and *homogeneous* to common catalysts [1]

example of heterogeneous, e.g. Fe (in the Haber process) linked to correct system [1]
equation, e.g. $N_2 + 3H_2 \longrightarrow 2NH_3$ [1]

how catalyst works, adsorption (onto the surface) [1]
ecf for non-iron catalyst

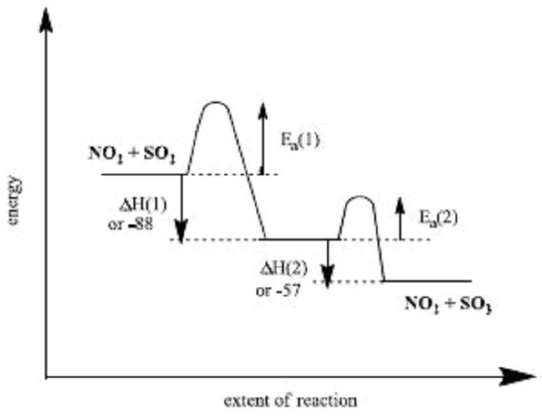
example of homogeneous, e.g. Fe^{3+} or Fe^{2+} (in $S_2O_8^{2-} + I^-$) linked to correct system [1]

equation, e.g. $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$ [1]

how catalyst works, e.g. $Fe^{3+} + I^- \longrightarrow Fe^{2+} + ½I_2$ [1]
ecf for non-iron catalyst

[8]

(b)



both E_a shown, with $E_a(1) > E_a(2)$ [1]
both ΔH shown, with $\Delta H(1) > \Delta H(2)$ [1]

[2]

[Total: 10]

Q20.

2 **(a)** catalyst: any two from the following three bullets for [1] mark:

- speeds up/increases (NOT alters or changes) the rate of a reaction
- lowers energy barrier/E_{act} **or** offers a lower energy pathway
- is not used up **or** remains unchanged **or** does not alter its mass/concentration **or** does not appear in stoichiometric equation **or** is regenerated [1]

homogeneous: (catalyst and reactants) in the same phase/state [1]

[Total: 2]

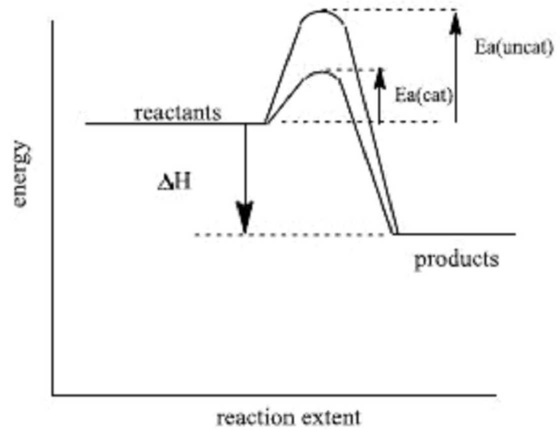
(b) **(i)** e.g. car exhausts/engines **or** aeroplanes **or** lightning **or** burning fuels **or** power stations [1]

nitrogen reacts with oxygen **or** $N_2 + O_2$ [1]

(ii) $NO_2 + SO_2 \longrightarrow NO + SO_3$
$NO + ½ O_2 \longrightarrow NO_2$
$SO_3 + H_2O \longrightarrow H_2SO_4$
$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$ **or** $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ (any 3 equations) 3 × [1]

[Total: 5]

(c)



ΔH shown as negative [1]
both E_a labelled and correct – i.e. for the forward reaction [1]
$E_a(cat) < E_a(uncat)$ [1]

[Total: 3]

Q21.

4 **(a)** (the energy change) when 1 mol of bonds [1]
is broken in the gas phase [1]

[2]

(b) **(i)** (C-X bond energy) decreases/becomes weaker (from F to I) [1]

due to bond becoming longer/not such efficient orbital overlap [1]

(ii) (as the bond energy of C-X decreases) the halogenalkanes become more reactive
(answer must imply that it is from F to I) [1]

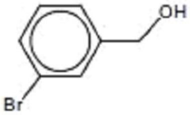
[3]

(c) The C-Cl bond is weaker than the C-F **and** C-H bonds
or C-Cl bond (E = 340) **and** C-H (E = 410) [1]

so is (easily) broken to form $Cl^\bullet$/Cl radicals/Cl atoms [1]
causing the breakdown of O_3 into O_2 [1]

[3]

(d) $Cl\text{-}CH_2CH_2\text{-}CO_2H$ [1]
$HO\text{-}CH_2CH_2CH_2\text{-}Cl$ [1]



[1]

[3]

(e) **(i)** light/UV/hν *or* 300°C [1]

(ii) (free) radical substitution [1]

(iii) ΔH = E(C-H) – E(H-Cl) = 410 – 431 = **–21** kJ mol^{-1} [1]

(iv) ΔH = E(C-H) – E(H-I) = 410 – 299 = **+111** kJ mol^{-1} ecf [1]

(v) The reaction with iodine is endothermic *or* ΔH is positive *or* requires energy [1]

(vi) $Cl_2 \longrightarrow \mathbf{2Cl^\bullet}$ [1]
$CH_3CH_2^\bullet + \mathbf{Cl_2} \longrightarrow \mathbf{CH_3CH_2Cl + Cl^\bullet}$ [1]
$\mathbf{CH_3CH_2^\bullet + Cl^\bullet} \longrightarrow CH_3CH_2Cl$ [1]

[8]

[Total: 19]

Q22.

3 **(a)** **(i)** $CH_3Br(g) \longrightarrow CH_3(g) + Br(g)$ [1]

(ii) $^1/_3\,AlCl_3(g) \longrightarrow {}^1/_3Al(g) + Cl(g)$ [2]
or $AlCl_3(g) \longrightarrow AlCl_2(g) + Cl(g)$
($AlCl_3(g) \longrightarrow Al(g) + 3Cl(g)$ for (1) mark)

[3]

(b) **(i)** bond energies decrease from Cl_2 to I_2 [1]
due to increasing bond length *or* increase in number of electron shells [1]
which causes less effective orbital overlap *or* less attraction for the shared pair [1]

(ii) *either* because fluorine is electronegative, (hence each F wants to keep its electrons to itself)
or because the bond length is so short there is repulsion between the lone pairs (on F)
or repulsion between the nuclei (of F) [1]

[4 max 3]

(c) **(i)** for chlorine:
$\Delta H = E(H-H) + E(Cl-Cl) - 2E(H-Cl) = 436 + 242 - (2 \times 431)$
$= \mathbf{-184}\ kJ\ mol^{-1}$ [2]
for iodine:
$\Delta H = E(H-H) + E(I-I) - 2E(H-I) = 436 + 151 - (2 \times 299)$
$= \mathbf{-11}\ kJ\ mol^{-1}$ [1]

(ii) Hydrides become less thermally stable down the group from Cl to I [1]
as the H–X bond energy decreases (more than does the X–X bond energy) [1]

[5]

(d) **(i)**

	Na	**O**	**Br**	
	15.2 / 23	31.8 / 16	53.0 / 79.9	[1]
	⇒ 0.661	1.99	0.663	
÷ 0.661⇒	1.0	3.0	1.0	

thus $\mathbf{NaBrO_3}$ [1]

(ii) $3Br_2 + 6NaOH \longrightarrow NaBrO_3 + 5NaBr + 3H_2O$
or $3Br_2 + 6OH^- \longrightarrow BrO_3^- + 5Br^- + 3H_2O$

species [1]
balancing [1]
[4]

[Total: 15]