**1.** (a) Many more ways of arranging / more disordered gas molecules than solid (particles) 1

(b) $\Delta S^{\ominus}_{system}$ = +123.7 + 2(+192.3) + 2(+69.9) – (+99.7) – 2(+94.6)
= +359(.2) J K$^{-1}$ mol$^{-1}$
Method **(1)** 2
Sign, value, units **(1)**

(c) $\Delta S^{\ominus}_{surroundings} = \dfrac{-\Delta H}{T}$ / = $\dfrac{-(+51.1\times10^{3})}{298}$ **(1)**
**= –** 171.5 / 171 J K$^{-1}$mol$^{-1}$ **(1)** 2

(d) $\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surroundings}$ So the total entropy change has a positive value / is greater than zero.

**OR**

$\Delta S^{\ominus}_{total}$ = **+** 187.7 / +188 J K$^{-1}$mol$^{-1}$ 1

(e) $0 = 359.2 - \dfrac{51.1\times10^{3}}{T}$

*Some recognisable correct method* **(1)**
*T* = 142(.3) / 143 K **(1)** 2

**[8]**

**2.** (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 J mol$^{-1}$ 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)** |
| $= -1560 / 1559$ J mol$^{-1}$ K$^{-1}$ | $= -238(.3)$ J mol$^{-1}$ 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)

| | |
|---|---|
| $\Delta S^{\ominus}_{total} = +174.8 - 1558.7$ <br> $= -1384 / -1380$ J mol$^{-1}$ K$^{-1}$ <br> *IF* $+ 174.8 - 1560$ <br> $= -1385(.2)$ <br> $= -1385 / 1390$ J mol$^{-1}$ K$^{-1}$ <br> *IF* $+ 174.8 - 1559$ <br> $= -1384$ J mol$^{-1}$ K$^{-1}$ | **=** $-63.5 / 64 / 63 / 63.2 / 63.4$ J mol$^{-1}$ 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) $K_p = p\ \text{co}_2$ ((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]**

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

**[13]**

**4.** (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 J $mol^{-1}K^{-1}$
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 kJ $mol^{-1}$ $K^{-1}$ / +433 J $mol^{-1}$ $K^{-1}$/+ 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 J $mol^{-1}$ $K^{-1}$/ +214 J $mol^{-1}$ $K^{-1}$/ +0.214 kJ $mol^{-1}K^{-1}$ **(1)**
**Positive** so **possible (1)** 2

(b) (i) Temperature

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)**
$K_p = (125)/55 \times 20^2$
$= 5.68 \times 10^{-3}$ / $5.7 \times 10^{-3}$ $\text{atm}^{-2}$ **(1)** 2

(c) (i) Number of molecules / fraction of molecules with energy ≥ $E_A$ /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]**

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

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

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

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

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

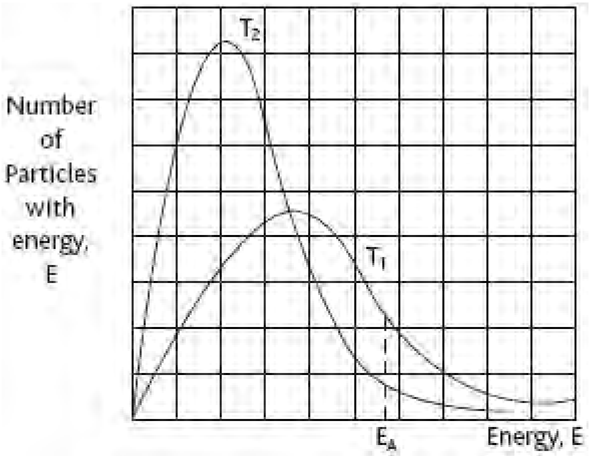
(d) (i) Higher T makes $\Delta S_{surroundings}$ decrease (so $\Delta S_{total}$ is less positive) 1

(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]**

**6.** (a) (i)



Starts at zero and approaching *x*-axis **(1)**
Maximum greater and at lower energy**(1)** – *$T_2$ needs only to be just higher than $T_1$*
*$T_2$ curve must go below $T_1$ curve approaching the x-axis* 2

(ii) As the temperature increases the energy of the particles increases **(1)**

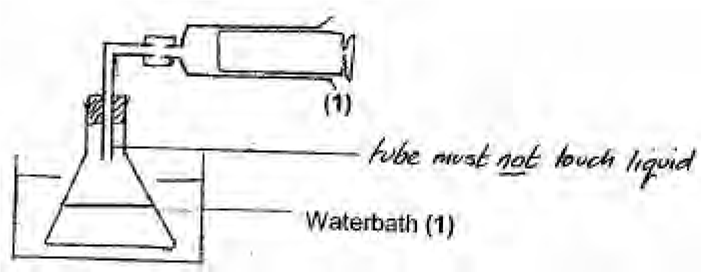
Use the diagram shading areas
*OR* more particles to the right hand side of $E_A$ line **(1)**

and so more (successful) collisions/particles have energy greater / equal or greater than the activation energy **(1)**
*NOT* "equal" *on its own*
*NOT mention of "frequency of collisions" on its own* 3

(iii) A catalyst provides an alternative route with a lower activation energy/ which requires less energy **(1)**

so more collisions / particles have energy greater than the activation energy **(1)** 2

(b) (i) e.g.



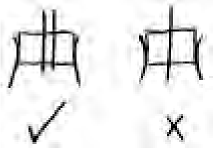
Measure the volume of gas given off in a given time / count bubbles / obscuring cross using limewater **(1)**

and then repeat over a range of temperatures **(1)**

**No diagram max 3**

*If method shown cannot possibly work* **max 1** *ie waterbath or sensible range of temperatures BUT NOT different temperatures*

Penalty
–1 for poor diagram



4

(ii) Positive

1 mol goes to 4 moles/particles (so more disorder) /increase in number of moles/particles **(1)**

products include a gas (and so more disorder) **(1)**

*NOT* 1 mole of compound/element goes to 4 moles of compound/element

If "negative" **0 (out of 2)** 2

(iii) Positive *with some explanation* e.g. $\Delta S_{surroundings} = -\Delta H/T$ *OR* because reaction is exothermic **(1)**

$\Delta H$ is therefore negative and so $\Delta S_{surroundings}$ must be positive **(1)**
*If negative given in (ii) allow TE here* 2

**[15]**

**7.** (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) $\Delta S^{\ominus}_{\text{surroundings}} = -\Delta H/T$ **(1)** For equation or use of equation
$= 191\,000 / 323$
$= (+)\ 591\ \text{J mol}^{-1}\text{K}^{-1}$ **(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) $\Delta S^{\ominus}_{\text{total}}$ 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

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

*2*$^{nd}$ *mark must be to at least 3 SF or working must be shown ie some evidence that ÷ their total number of moles*

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

*Units marked independently*
*ALLOW* $2.5 \times 10^{-3}$
*Many have total number of moles as 100 even when it is not – ALLOW TE for 2nd and 3*$^{rd}$ *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* $2.60 \times 10^{-3}$*]* 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 $\Delta S^{\ominus}_{\text{surroundings}}$ will become less positive/more negative as the temperature is increased (and $\Delta S_{\text{system}}$ will remain almost unchanged) so $\Delta S_{\text{total}}$ becomes negative for the forward reaction **(1)** 2

**[16]**

**8.** (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)**

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

*OR*

$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ [*OR given in words*]
as reaction goes, $\Delta S_{\text{total}}$ must be positive therefore $\Delta S_{\text{surroundings}}$ must be positive

*OR*

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

(b) (i) $$(\text{Kp}) = \frac{{P_{NO_2}}^2}{{P_{NO}}^2 \times P_{O_2}}$$ **(1)**

*Check that it is* ***not*** *a "+" on denominator.*

*ALLOW (   ) but NOT [   ]* eg *ALLOW* $((P_{NO_2})^2)^2$ etc

*ALLOW* $(pNO_2)^2$

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

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

*NOT* $\text{atm}^{-}$*etc*

*NOT* $\text{Kpa}^{-1}$ 2

(ii) Temperature

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

but the lower temperature may slow the reaction down too much *OR reverse argument* **(1)**

Pressure

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

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

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

*To award any of the yield marks must say why* 4

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

Eg

The pressure could be measured **(1)**

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

*OR* colour **(1)**

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

*OR* total volume **(1)**

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

*ALLOW* acidity because $NO_2$ 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]**

**9.** (a) **Any 2**
Measure the loss in mass as a gas/carbon dioxide is given off **(1)**

Measure the concentration of the acid by titration
*OR* Carry out a titration with sodium hydroxide **(1)**
*NOT* “titration” on its own

Measure conductivity because 4 ions go to 3 ions / decrease in ions / change in number of ions **(1)**

Measure pH because acid is used up / changes / concentration changes /one reactant is acidic **(1)**

*NOT* dilatometry / nmr / x-ray crystallography / temperature change / colorimetry / indicator / change in mass of $CaCO_3$ 2

(b) Initially some carbon dioxide dissolves in the solution (until the solution is saturated).
*OR*
Some $CO_2$ might escape whilst adding acid/before putting on bung 1

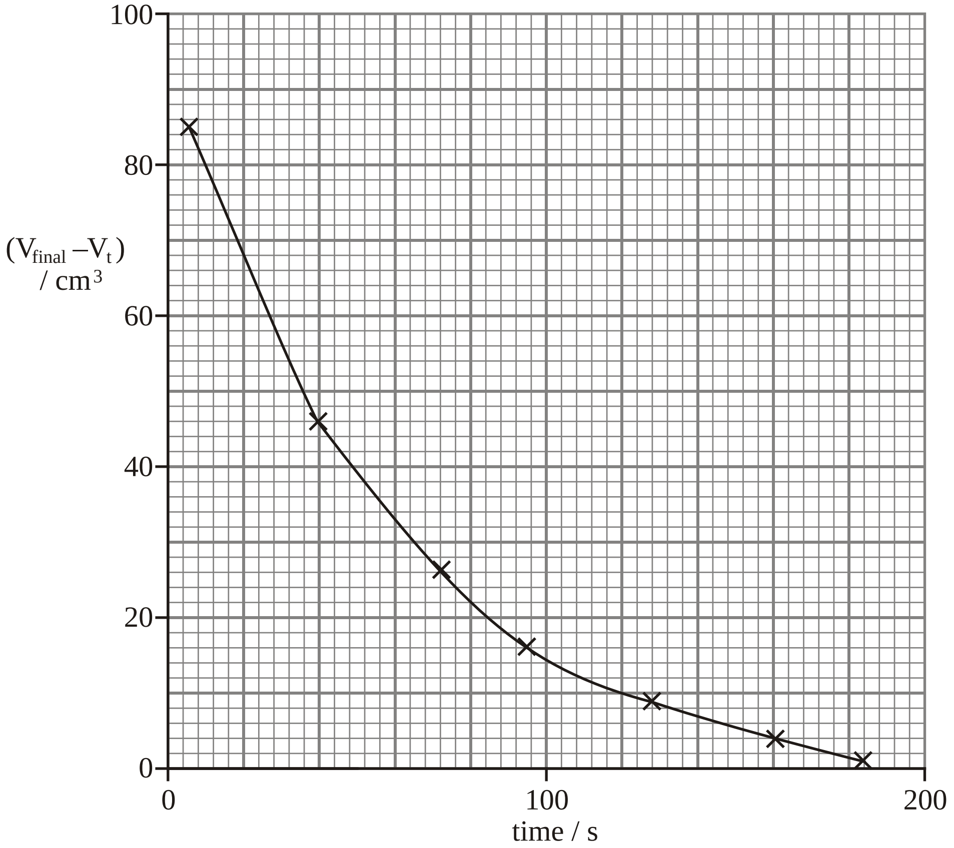
(c) (i) 88 ($cm^3$) 1

(ii)

| | | | |
|---|---|---|---|
| 95 | 72 | **16** | |
| 125 | 79 | **9** | |
| 155 | 84 | **4** | |
| 185 | 87 | **1** | 1 |

(iii) The concentration of the hydrochloric acid / HCl
*OR* [HCl]
*NOT* concentration of reactants 1

(iv)



*ALLOW extrapolated back to between 88 and 100*

points correctly plotted **(1)**
*ALLOW* TE for points

and reasonably smooth curve drawn **(1)** 2
*NOT* dot-to-dot

(v) three **successive** half-lives shown on the graph **(1)**
*MUST start at defined volume NOT* 0s/85 cm$^3$

all three values similar about 37s **(1)**
*ALLOW* 32-42 or show on graph
*NOT* 40, 80, 120

constant half-life / half-life not increasing means first order reaction **(1)**

*If only two half lives shown **max 2***
*If in (v) zero / 2$^{nd}$ order deduced **max 1** for first part but TE allowed to parts (vi) and (vii)* 3

(vi) rate = k[HCl]
*OR* rate =k[HCl]$^1$
*OR* rate =K[HCl]$^1$[CaCO$_3$]$^0$
*NOT* rate = k[V$_{final}$-V$_t$]$^1$

If zero order
rate = k
*OR* rate = k[HCl]$^0$
If second order
rate = k [HCl]$^2$
*NOT* rate = k[CaCO$_3$]$^1$[HCl]$^1$ 1

(vii) s$^{-1}$

T.E zero order – mol dm$^{-3}$ s$^{-1}$

second order – dm$^3$ mol$^{-1}$ s$^{-1}$ 1

(d) Δ**S**$_{system}$
positive + some sensible reason eg gas given off **(1)**
as a mole of a gas given off and three moles including one solid becomes three moles with no solid / gas more random than solid
*OR*
Gas more disordered than a solid

*OR*
Despite same number of moles/particles **(1)**

Δ**S**$_{total}$

positive + some reason **(1)**
eg
positive because reaction exothermic / favourable **(1)**

positive + good reason **(2)**
*eg*
positive because reaction is spontaneous / goes to completion / feasible
OR Δ**S**$_{surroundings}$ is positive because ΔH is negative /
reaction exothermic ∴ ΔS$_{total}$ positive **(2)** 4
[provided ΔS$_{system}$ shown positive earlier]

**[17]**

**10.** (a) (i) $NO_2$ is a gas (whereas BaO is a solid) **(1)**
$Ba(NO_3)_2$ has a more complicated structure than BaO **(1)**
Allow 2nd mark if a correct statement is combined with a "neutral" wrong statement 2

*Accept $Ba(NO_3)_2$ "molecule" has more electrons / is larger than BaO "molecule" **(1)***

*Accept more atoms/ions/particles*

*Accept more complicated/complex compound*

*Reject $Ba(NO_3)_2$ has a larger molar mass than BaO*

*Reject more molecules/elements*

(ii) $\Delta S^{\ominus}_{\text{system}} = 70.4 + (2 \times 240.0) + (½ \times 205.0) – 213.8$ **(1)**
$= +439.1\ \text{J mol}^{-1}\ \text{K}^{-1}$ **(1)**
–1 per error 2

*Accept +439 J $mol^{-1}$ $K^{-1}$*

*Accept J/ mol /K*

(b) $\Delta S^{\ominus}_{\text{surroundings}} = -\dfrac{\Delta H}{T}$ **(1)** $= -\dfrac{505 \times 1000}{298}$
$= – 1700\ \text{J mol}^{-1}\ \text{K}^{-1}$ (3 s.f.) **(1)**
Penalise wrong units in (a)(ii) and (b) once only 2

*Accept –1690 J $mol^{-1}$ K–*
*Accept –1695 J $mol^{-1}$ $K^{-1}$*
*Answers in kJ $mol^{-1}$ $K^{-1}$*

*Reject –1694 J $mol^{-1}$ $K^{-1}$*
*Reject –1694.6 J $mol^{-1}$ $K^{-1}$*
*Reject –1694.63 J $mol^{-1}$ $K^{-1}$*

(c) $\Delta S^{\ominus}_{\text{total}} = +439.1 – 1695 = – 1260\ (\text{J mol}^{-1}\ \text{K}^{-1})$ **(1)**
*Allow TE [follow through working from (a)(ii) and (b)]*
Mark consistently with (a)(ii) and (b)
The reaction isn't spontaneous / doesn't "go" (at 298K) **(1)**
Must be consistent with sign in calculation 2

*Accept –1256 J $mol^{-1}$ $K^{-1}$*
*Accept –1261 J $mol^{-1}$ $K^{-1}$*
*Accept –1255.5 J $mol^{-1}$ $K^{-1}$*

(d) When just spontaneous, $\Delta S^{\ominus}_{total} = 0$

or implied by calculation i.e $\frac{505 \text{ OR } 505000}{\text{a(ii)}}$ **(1)**

$\Rightarrow \Delta S^{\ominus}_{surroundings} = -439.1 \text{ J mol}^{-1} \text{ K}^{-1}$

$\Rightarrow T = \frac{505 \times 1000}{439.1} = 1150 \text{ (K)}$ **(1)**

*Accept 1150.1 K*
*Accept 877 °C*
*Accept 1151K with no working (1 max)*

*Reject 1151K for 2nd mark*
*Reject any negative value for T (in K): no 2nd mark*
*Reject 1150 °C*

ignore $^{0}$K
Allow full marks for an answer without working 2

**[10]**

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

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

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

*Accept + 806 J mol K$^{-1}$*

(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 $mol^{-1}$ $K^{-1}$/$\Delta S_{tot}$ 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) $K_p = \frac{pNO_2{}^2}{pNO^2 \times pO_2}$ 1

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

*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]**

**12.** (a) $\Delta S^\ominus_{system} = [202.9 + 2 \times 192.3] - [99.7 + 2 \times 94.6]$
$= 587.5 - 288.9 = +299$ J mol$^{-1}$ K$^{-1}$
Value **(1)** sign & units **(1)**

Allow TE for internal error only if a failure to double one or both of the two energies:
i.e. +106/+106.3 J mol$^{-1}$ K$^{-1}$
+393/+393.2 J mol$^{-1}$ K$^{-1}$
+201/+200.9 J mol$^{-1}$ K$^{-1}$ **(1 max)** 2

*Accept +298.6 J mol$^{-1}$ K$^{-1}$* ***(2)***

*Accept correct answer with no working* ***(2)***

*No credit for answer based on an inverse subtraction, i.e. –299/–298.6 J mol$^{-1}$ K$^{-1}$*

(b) $\Delta S^\ominus_{surroundings} = -\Delta H/T$ or $-21200/298$ **(1)**
$= -71.1$ J mol$^{-1}$ K$^{-1}$ **(1)**

Only penalise units once in (a) & (b)
Allow **one minor** slip in units, e.g. J mol$^{-}$ K$^{-1}$ 2

*Accept correct answer with no working* ***(2)***

*Accept –0.0711 kJ mol$^{-1}$ K$^{-1}$*

*Reject all other values*

(c) (i) $\Delta S^{\ominus}_{\text{total}}$ = (+)227.5 (J mol$^{-1}$ K$^{-1}$) / answer to (a) plus answer to (b), provided that value is positive.

Since value is positive, (reaction is spontaneous)
Must do the arithmetic
**Both needed for the mark** 1

*Accept rounded value e.g.*
*(+)228 J mol$^{-1}$ K$^{-1}$*

*Accept $\Delta S^{\ominus}_{system}$ is large and +ve*
*Accept $\Delta S^{\ominus}_{surroundings}$ is small and –ve*
*so $\Delta S^{\ominus}_{total}$ must be positive (and reaction is spontaneous)*

*Reject any negative number*

(ii) Activation energy must be high / reaction must be kinetically hindered/reaction doesn’t have to be fast 1

*Accept poor contact between solids*
*Accept few/no collisions between particles*

*Reject $\Delta H$ is positive, so heat is needed to start the reaction*

(iii) Dissolve solid(s) in water/solvent (before “mixing”) **(1)**

*Accept grind into a (fine) powder*

*Reject use of a catalyst*

Particles/ions/”molecules” (**not** atoms) become mobile, so increasing chance of collisions, (hence interactions) **(1)**

**mark independently** 2

*Accept which increases surface area so* ***improves chance of collisions***

**[8]**

**13.** (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 $3.16 \times 10^{-16}$ (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* $\mathbf{2 \times} p_{NO}$

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

$K_p$ remains constant/is (still) $5.0 \times 10^{-31}$ **(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) (Δ*H* 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 $\Delta S_{total}$ (also) becomes greater/less negative/more positive/increases 1

*Accept* $\Delta S_{surroundings}$ *becomes “smaller”, if qualified, e.g. becomes closer to zero*

(d) Equilibrium might not have been reached (in the very short time the gases are present in the engine)

Ignore references to the fact that the system is not “closed” 1

*Accept other gases are present in the air (apart from* $N_2$ *and* $O_2$*)*

*Accept temperature inside engine may be less than 1500K*

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

**[12]**

**14.** (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* $\text{mol}^{-1}\ \text{K}^{-1}$

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

*Accept final answer with no working* ***(2)***

*Allow "j" for "J"*

*Reject full calculator display eg –415.4362416*

*Reject more than 2 dp e.g. –415.436*

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

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

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

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

OR
Equilibrium completely to the left 1

*ALLOW TE from (c)(i)*

(d) (i) $K_p = \frac{p_{PCl_3} \times p_{CL_2}}{p_{PCl_5}}$ **(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<br>(1)** | | $\mathbf{\frac{0.15}{0.25} \times 4.32}$<br>**= 2.592** |
| $PCl_3$(g) | | **0.05** | $\mathbf{\frac{0.05}{0.25} \times 4.32}$<br>**= 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 4*$^{th}$ *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]**

**15.** (a) B 1

(b) A 1

**[2]**

**16.** (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
$20 \times 4.18 \times \Delta T = 1\,946$ **(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]**